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on April 18, 2002

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PATENT

#02-0055-UNI
Case #C7602(V)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Adriaanse et al.
Serial No.: 10/084,799
Filed: February 26, 2002
For: LIQUID CLEANING COMPOSITIONS AND THEIR USE

Edgewater, New Jersey 07020
April 18, 2002

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Sir:

Pursuant to rule 55(b) of the Rules of Practice in Patent Cases, Applicant(s) is/are submitting herewith a certified copy of the Great Britain Application No. 0104980.8 filed February 28, 2001, upon which the claim for priority under 35 U.S.C. § 119 was made in the United States.

It is respectfully requested that the priority document be made part of the file history.

Respectfully submitted,

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1. Your reference	RMW/C7602(V)		
2. Patent application number (The Patent Office will fill in this part)	<div style="text-align: right;">0104980.8</div> <div style="text-align: right;">28 FEB 2001</div>		
3. Full name, address and postcode of the or of each applicant (underline all surnames)	Unilever PLC Unilever House Blackfriars London EC4P 4BQ UNITED KINGDOM		
Patents ADP number (if you know it)			
If the applicant is a corporate body, give the Country/state of its incorporation	UNITED KINGDOM		
4. Title of the invention	LIQUID CLEANING COMPOSITIONS AND THEIR USE		
5. Name of your agent (if you have one)	LLOYD WISE, TREGEAR & CO COMMONWEALTH HOUSE 1-19 NEW OXFORD STREET LONDON WC1A 1LW ENGLAND		
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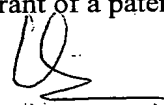
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LIQUID CLEANING COMPOSITIONS AND THEIR USE

FIELD OF INVENTION

- 5 The present invention relates to liquid cleaning compositions containing proteolytic enzymes and stabilising systems for those enzymes. It also relates to methods of using such compositions for the cleaning of substrates.

BACKGROUND OF INVENTION

10

In liquid detergent compositions, especially those for the washing of textile fabrics, it is common to include one or more enzymes for assisting removal of various kind of soil. Amongst these are proteolytic enzymes, often referred to as "proteases". Proteases are used to assist in removal of protein-based soil. However, the very nature and activity of these enzymes means that that they attack any other component in the liquid composition which has a protein-like structure. As a result, they can degrade other enzymes in the liquid, as well as undergoing self-degradation. To counteract this, it is usual also to incorporate an enzyme stabilising system. Such stabiliser systems commonly consist of a boron compound, eg. borax, together with a polyol, eg. glycerol or sorbitol. These two components are believed to form an enzyme-inhibiting complex which dissociates at the pH of the wash liquor, disabling the inhibiting effect so that the protease can act upon the proteins soil.

15

20

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Other protease stabilisers such as calcium chloride/calcium formate are also known but are not as effective as those systems based on boron. However, for environmental reasons, it is desired to reduce the amount of boron in the composition.

30

The specification of WO 00/12677 discloses compositions and methods for catalytically bleaching substrates with atmospheric oxygen, using a metal-ligand complex as catalyst. These complexes allow catalytic bleaching by atmospheric oxygen without inclusion of peroxygen bleaches.

Peroxygen bleaches are well known for their ability to remove stains from substrates. Traditionally, the- substrate is subjected to hydrogen peroxide, or to substances which

can generate hydroperoxyl radicals, such as inorganic or organic peroxides. Generally, these systems must be activated. One method of activation is to employ wash temperatures of 60°C or higher. However, these high temperatures often lead to inefficient cleaning, and can also cause premature damage to the substrate.

5

A preferred approach to generating hydroperoxyl bleach species is the use of inorganic peroxides coupled with organic precursor compounds. These systems are employed for many commercial laundry powders. For example, various European systems are based on tetraacetyl ethylenediamine (TAED) as the organic precursor coupled with sodium perborate or sodium percarbonate, whereas in the United States laundry bleach products are typically based on sodium nonanoyloxybenzenesulphonate (SNOBS) as the organic precursor coupled with sodium perborate.

10

15

In conventional liquid detergent compositions, it has long been known that peroxygen bleaches and enzymes interact such that they cannot be incorporated together and yet remain stable. A number of ways of mitigating this unwanted interaction have been described but they are either costly and difficult to implement or are only partially successful.

20

Since the atmospheric oxygen bleach catalysts work to catalyse bleaching activity of the dissolved atmospheric oxygen in any liquid in which they are incorporated, it can be expected that in liquid detergent compositions containing enzymes, they will catalyse the dissolved oxygen to attack those enzymes. However, surprisingly, the atmospheric oxygen bleach catalysts, and indeed the ligands from which the corresponding metal complex catalysts are formed, boost the stabilising effect of conventional kinds of enzyme stabiliser. This enables the amount of conventional stabiliser to be reduced.

25

30

WO-A-00/52124 discloses cross-bridged maropolycyclic ligands in complex with a transition metal, as a bleach catalysts. Some examples are liquid compositions which also contain protease and an enzyme stabilising system which includes sodium metaborate. These are relatively strongly alkaline compositions. There is no disclosure of the ability of the catalyst to enhance the stabilising performance of the bleach stabilising system.

SUMMARY OF INVENTION

Accordingly, in a first aspect, the present invention provides an aqueous liquid cleaning composition having a pH of at least 7, preferably from 7 to 11, more preferably from 7 to 10 and comprising a proteolytic enzyme and a primary stabiliser therefor, the composition further comprising an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen.

A second aspect of the invention provides an aqueous liquid cleaning composition comprising a proteolytic enzyme and a non-boron primary stabiliser therefor, the composition further comprising an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen, the composition being substantially free of boron enzyme stabiliser.

In a third aspect, the present invention provides a method of cleaning a substrate, comprising applying to the substrate an aqueous liquid cleaning composition according to the first and/or second aspect of the invention.

Furthermore, in a fourth aspect, the present invention provides the use of an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen, as a secondary enzyme stabiliser in an aqueous liquid detergent composition comprising a proteolytic enzyme and a primary stabiliser therefor.

A fifth aspect, the present invention provides a method of treating a substrate by contacting the substrate with an aqueous liquid detergent cleaning according to the first and/or second aspect of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The Liquid Detergent Composition

- 5 Liquid detergent compositions generally can be considered either to be isotropic or structured.

The liquid cleaning composition may be formulated as a concentrated cleaning liquid for direct application to a substrate, or for application to a substrate following dilution, such
10 as dilution before or during use of the liquid composition by the consumer or in washing apparatus.

Whilst the composition and method according to the present invention may be used for cleaning any suitable substrate, the preferred substrate is a laundry fabric. Cleaning may
15 be carried out by simply leaving the substrate in contact for a sufficient period of time with a bleach medium constituted by or prepared from the liquid cleaning composition. Preferably, however, the cleaning medium on or containing the substrate is agitated.

Product Form

20 The liquid cleaning composition according the present invention is preferably a concentrated liquid cleaning composition. In one aspect of the invention the liquid cleaning composition is isotropic. In another aspect of the invention the liquid detergent composition is structured. It should be understood that the liquid compositions according
25 to any aspect of the present invention have a physical form which preferably ranges from a pourable liquid, a pourable gel to a non-pourable gel. These forms are conveniently characterised by the product viscosity. In these definitions, and unless indicated explicitly to the contrary, throughout this specification, all stated viscosities are those measured at a shear rate of 21 s^{-1} and at a temperature of 25°C .

30 Compositions according to any aspect of the present invention preferably have a viscosity of no more than $1,500 \text{ mPa.s}$, more preferably no more than $1,000 \text{ mPa.s}$, still more preferably, no more than 500 mPa.s .

Compositions according to any aspect of the present invention which are pourable gels, preferably have a viscosity of at least 1,500 mPa.s but no more than 6,000 mPa.s, more preferably no more than 4,000 mPa.s, still more preferably no more than 3,000 mPa.s and especially no more than 2,000 mPa.s.

5

Compositions according to any aspect of the present invention which are non-pourable gels, preferably have a viscosity of at least 6,000 mPa.s but no more than 12,000 mPa.s, more preferably no more than 10,000 mPa.s, still more preferably no more than 8,000 mPa.s and especially no more than 7,000 mPa.s.

10

Physically stable

For the purpose of this invention a composition is physically stable when less than 2% phase separation occurs after 2 week storage at 37°C. With isotropic liquids this phase separation generally starts with the liquid becoming hazy.

15

Water

Preferably the amount of water in the liquid detergent composition is from 5 to 95%, more preferred from 25 to 75%, most preferred from 30 to 50%. Especially preferred less than 45% by weight.

20

I Isotropic liquid cleaning compositions

Isotropic liquid cleaning compositions are defined for the present purpose as liquid detergent compositions wherein the surfactants do not form liquid crystalline phases, like multilamellar droplets of surfactant material. Isotropic liquids are generally not birefringent under static conditions but may be birefringent under flow.

25

30 *Ia Surfactant*

The isotropic compositions herein comprise from 1 to 90%, preferably from 10 to 70% by weight of an anionic, nonionic, cationic, zwitterionic active detergent material or mixtures

thereof. Preferably the compositions herein comprise 12 to 60 % of surfactant, more preferably 15 to 40%.

Non-limiting examples of other surfactants useful herein typically at levels from about 10 % to about 70%, by weight, include the conventional C11-C18 alkylbenzenesulphonates ("LAS"), the C10-C18 secondary (2,3) alkyl sulphates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3\text{-M}^+)\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3\text{-M}^+)\text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilising cation, especially sodium, unsaturated sulphates such as oleyl sulphate, C10-C18 alkyl alkoxy carboxylates (especially the EO 1-7 ethoxycarboxylates), the C10-C18 glycerol ethers, the C10-C18 alkyl polyglycosides and their corresponding sulphated polyglycosides, and C12-C18 alpha-sulphonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulphobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used.

Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Other anionic surfactants useful for deterative purposes can also be included in the isotropic compositions hereof. These can include salts (including, for example, sodium potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C9-C20 linear alkylbenzenesulphonates, C8-C22 primary or secondary alkanesulphonates, C8-C24 olefinsulphonates, sulphonated polycarboxylic acids, alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphates, alkyl phenol ethylene oxide ether sulphates, paraffin sulphonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinamates and sulphosuccinates, monoesters of

5 sulphosuccinate (especially saturated and unsaturated C12-C18 monoesters) diesters of sulphosuccinate (especially saturated and unsaturated C6-C14 diesters), N-acyl sarcosinates, sulphates of alkylpolysaccharides such as the sulphates of alkylpolyglucoside, branched primary alkyl sulphates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO-M^+$ wherein R is a C8-C22 alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralised with sodium hydroxide. Further examples are given in Surface Active Agents and Detergents (Vol. I and II by Schwartz, Perry and Berch).

10 The isotropic compositions of the present invention preferably comprise at least about 5%, preferably at least 10%, more preferably at least 12% and less than 70%, more preferably less than 60% by weight, of an anionic surfactant.

15 Alkyl sulphate surfactants, either primary or secondary, are a type of anionic surfactant of importance for use herein. Alkyl sulphates have the general formula ROS_3M wherein R preferably is a C10-C24 hydrocarbyl, preferably an alkyl straight or branched chain or hydroxyalkyl having a C10-C20 alkyl component, more preferably a C12-C18 alkyl or hydroxyalkyl, and M is hydrogen or a water soluble cation, e.g., an alkali metal cation (e.g., sodium potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., 20 tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like.

25 Typically, alkyl chains of C12-C16 are preferred for lower wash temperatures (e.g., below about 50°C and C16-C18 alkyl chains are preferred for higher wash temperatures (e.g., about 50°C).

30 Alkyl alkoxyated sulphate surfactants are another category of preferred anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C10-C24 alkyl or hydroxyalkyl group having a C10-C24 alkyl component, preferably a C12-C20 alkyl or hydroxyalkyl, more preferably C12-C18 alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is

greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is hydrogen or a water soluble cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulphates as well as alkyl propoxylated sulphates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines, e.g., monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C12-C18 alkyl polyethoxylate (1.0) sulphate, C12- C18 alkyl polyethoxylate (2.25) sulphate, C12-C18 alkyl polyethoxylate (3.0) sulphate, and C12-C18 alkyl polyethoxylate (4.0) sulphate wherein M is conveniently selected from sodium and potassium.

The isotropic compositions of the present invention preferably comprise at least about 5%, preferably at least 10%, more preferably at least 12% and less than 70%, more preferably less than 60% by weight, of a nonionic surfactant.

Preferred nonionic surfactants such as C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C6 to C12 alkyl phenols, alkylene oxide condensates of C8-C22 alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present isotropic compositions. An extensive disclosure of these types of surfactants is found in U.S. Pat. 3,929,678.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 are also preferred nonionic surfactants in the isotropic compositions of the invention.

Further preferred nonionic surfactants are the polyhydroxy fatty acid amides.

A particularly desirable surfactant of this type for use in the isotropic compositions herein is alkyl-N-methyl glucamide.

Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C12-C18 glucamides can be used for low sudsing. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used.

5

Another preferred anionic surfactant is a salt of fatty acids. Examples of fatty acids suitable for use of the present invention include pure or hardened fatty acids derived from palmitoleic, safflower, sunflower, soybean, oleic, linoleic, linolenic, ricinoleic, rapeseed oil or mixtures thereof. Mixtures of saturated and unsaturated fatty acids can also be used herein.

10

It will be recognised that the fatty acid will be present in the liquid detergent isotropic composition primarily in the form of a soap. Suitable cations include, sodium, potassium, ammonium, monoethanol ammonium diethanol ammonium, triethanol ammonium, tetraalkyl ammonium, e.g., tetra methyl ammonium up totetradecyl ammonium etc. cations.

15

The amount of fatty acid will vary depending on the particular characteristics desired in the final detergent isotropic composition. Preferably 0 to 30%, more preferably 1-20 most preferably 5-15% fatty acid is present in the inventive isotropic composition.

20

Ib carriers

Isotropic liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilising surfactant. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

25

Ic Clarity

The clarity of the isotropic compositions according to the present invention does not preclude the isotropic composition being coloured, e.g. by addition of a dye, provided that it does not detract substantially from clarity. Moreover, an opacifier could be included to reduce clarity if required to appeal to the consumer. In that case the definition of clarity

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applied to the isotropic composition according to any aspect of the invention will apply to the base (equivalent) isotropic composition without the opacifier.

5 II Structured liquid cleaning compositions

Ila Form of Structuring

10 Conventionally, liquid cleaning compositions may be structured in one of two different ways to endow consumer-preferred flow behaviour and/or turbid appearance and/or of suspending particulate solids such as detergency builders or abrasive particles.

15 The first way is to employ an "external structurant" such as a gum or polymer thickener. The second way is to form a lamellar phase "internal structure" from the surfactant(s) and water, the latter usually containing dissolved electrolyte.

20 Lamellar phases are a particular class of surfactant structures which, *inter alia*, are already known from a variety of references, e.g. H.A. Barnes, 'Detergents', Ch.2 in K.Walters (Ed), Rheometry: Industrial Applications', J. Wiley & Sons, Letchworth 1980.

25 Lamellar phases can themselves be considered as divided into the sub-classes planar lamellar phases and lamellar droplets. Products can contain exclusively planar lamellar phases or exclusively lamellar droplets or the two forms can co-exist in the same product.

30 The presence of lamellar phases in a liquid detergent product may be detected by means known to those skilled in the art, for example optical techniques, various rheometrical measurements, X-ray or neutron diffraction, and electron microscopy.

35 Lamellar droplets consist of an onion-like configuration of concentric bi-layers of surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

Examples of internally structured liquids containing a dispersion of lamellar droplets but without suspended solids are given in US patent 4 244 840, whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US 4 244 840. Others are disclosed in
5 European Patent Specification EP-A-151 884, where the lamellar droplets are called 'spherulites'.

There are also known examples of products containing planar lamellar phases which may be extensive throughout the liquid or distributed as discrete layers interspersed with an
10 aqueous continuous phase. Planar lamellar phases are generally less well suited to combine suspending solid material with preferred flow properties than are lamellar droplets, but they are nevertheless eminently suitable for thickening the product or endowing it with other consumer-preferred properties.

15 Concentrated liquid cleaning compositions are more efficient in use and require less package and transport costs per wash. However, the high concentration of ingredients is often problematic. One problem is to formulate an internally structured composition that is physically stable over a prolonged period of time as the highly concentrated surfactants tend to aggregate whereby phase separation occurs. Moreover, because other
20 ingredients in the composition are also present in high concentrations, these ingredients may also separate out themselves or cause other ingredients to become insoluble.

One preferred embodiment of the present invention provides a structured detergent composition comprising

25 (a) from 1 to 90% preferably, from 10 to 70% of an anionic, nonionic, cationic, zwitterionic active detergent material or mixtures thereof,

(b) from 1 to 60% of a salting out electrolyte;

30 (c) from 0.001 to 10% of protease;

(d) from 2 to 40% of at least one saccharide selected from the group consisting of disaccharides and trisaccharides, derivatives thereof and mixtures thereof;

(e) 0 to 10% of deflocculating polymer; and

5 (f) less than 3% of an antioxidant selected from the group consisting of alkalimetalsulphites, alkalimetabisulphites, alkalimetabisulphites or alkalimetalthiosulphates.

The structured composition comprises less than 3 wt%, more preferably less than 2 wt%, most preferably less than 1 wt% of the antioxidant.

10

IIb Clarity

15 If the composition is lamellar structured, then the composition is preferably substantially unclear. Preferably, this means that the composition as an optical transmissivity of at less than 5% through a path length of 1cm at 25°C. These measurements may be obtained using a Perkin Elmer UV/VIS Spectrometer Lambda 12 or a Brinkman PC801 Colorimeter at a wavelength of 520nm, using water as the 100% standard.

20 *IIc Surfactant*

The structured compositions herein comprise from 1 to 90% by weight of an anionic, nonionic, cationic, zwitterionic active detergent material or mixtures thereof.

25 In the event that the structured composition is lamellar structured, the clarity of the lamellar phase may be controlled by choosing an appropriate surfactant or blend of surfactants. One suitable approach is to include aralkyl surfactants such as alkyl benzene sulphonates, i.e the total of aralkyl surfactants should more than 1%, preferably more than 5%, more preferably more than 10%, and especially more than 30% by weight
30 of the total surfactants (including any soap).

To formulate a surfactant blend suitable for forming a lamellar phase without using aralkyl materials, one may, for example, employ a blend of primary and/or secondary alkane sulphate or sulphonate material together with one or more nonionic surfactants.

Examples of suitable alkane sulph(on)ates are sodium and potassium alkyl sulphates, especially those obtained by sulphonating higher (C_8-C_{18}), primary or secondary alcohols produced, for example, from tallow or coconut oil.

5

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and reactive hydrogen atom, for example aliphatic alcohols, acids, amides with alkylene oxides, especially ethylene oxide, either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{18}) primary or

10

secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

15

Preferably, the weight ratio of the total alkane sulph(on)ate material to the total nonionic material is from 90:10 to 10:90, more preferably from 80:20 to 50:50.

Another suitable surfactant blend for this purpose comprises one or more soaps with one or more nonionic surfactants.

20

Suitable soaps include alkali metal soaps of long chain mono- or dicarboxylic acids for example one having from 12 to 18 carbon atoms. Typical acids of this kind are oleic acid, ricinoleic acid and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palm kernel oil or mixtures thereof. The sodium or potassium soaps of these acids

25

can be used.

Suitable nonionic surfactants to blend with the soap are mentioned above. Preferably, the weight ratio of the total soap to the total nonionic material is from 60:40 to 90:10, more preferably from 70:30 to 80:20.

30

In other preferred structured compositions, part or all of the detergent active material is a stabilising surfactant, which has an average alkyl chain length greater than 6 C-atoms, and which has a salting out resistance, greater than, or equal to 6.4. These stabilising surfactants are disclosed in EP-A-328 177. Examples of these materials are alkyl

polyalkoxylated phosphates, alkyl polyalkoxylated sulposuccinates; dialkyl diphenyloxide disulphonates; alkyl polysaccharides and mixtures thereof. The advantage of these surfactants is that they are surfactants with a relatively low refractive index and these surfactants tend to decrease the droplet size of the lamellar droplets. Both effects have a positive effect on the clarity of the systems.

However, aside from any desire to formulate the surfactant content to control the clarity of the lamellar structured composition, in the widest sense, the detergent-active material in the structured composition, in general, may comprise one or more surfactants, and may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, sub-classes and specific materials described in 'Surface Active Agents' Vol. 1, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

In many (but not all) cases, the total detergent-active material may be preferably present at from 10% to 70% by weight of the total structured composition, for example from 12% to 60% and typically from 15% to 40% by weight. However, one preferred class of structured compositions comprises at least 15%, most preferably at least 25% and especially at least 30% of detergent-active material based on the weight of the total structured composition. In the case of blends of surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids.

Common anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higheracyl radicals.

Aside from anionic surfactants already mentioned with regard to refractive index control, where appropriate, one may still employ conventional sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene

5 sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. Other suitable anionics include sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_6 - C_{18}) fatty
10 alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_{8-20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2
15 and then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10-20} alpha-olefins, with SO_3 and then neutralising and hydrolyzing the reaction product.

15 *IId Deflocculating Polymer*

In one preferred embodiment of the present invention when the composition is structured, the composition comprises from 0 to 10% of deflocculating polymer.

20 According to the specification of EP-A-346 995, the dependency of stability and/or viscosity upon volume fraction is favourably influenced by incorporating into the lamellar dispersion, a deflocculating polymer comprising a hydrophilic backbone and one or more hydrophobic side-chains.

25 The theory of function of these deflocculating polymers is that the hydrophobic chains are anchored in the outer bilayer of the lamellar droplet. The hydrophilic part is extended outwards. These hydrophilic 'brushes' are responsible for the steric stabilisation of the droplets, provided that the 'brushes' exceed a certain length. For surfactant blends in common use, the optimum length of the polymer hydrophobic chain, in order to be
30 anchored into the bilayer is in the order of C_{12} - C_{15} , about the length of the surfactants in the droplet.

Thus, it is already well known to incorporate deflocculating polymers in aqueous liquid detergents which are structured with lamellar droplet dispersions. However, in these

conventional structured compositions, the polymer is incorporated in a base composition (i.e. the same composition without the polymer) which is already stable and pourable. EP-A- 346 995 defines, in practical terms, the conventional deflocculating effect as that of a polymer in a stable and pourable composition whereby the equivalent composition minus the deflocculating polymer, has a significantly higher viscosity and/or becomes unstable.

Preferably, the term "does not have significantly higher viscosity" means that a shear rate of 21s^{-1} , the difference in viscosity is no more than 500mPa.s , preferably no more than 250mPa.s .

Preferably, the term "stable" means that the structured liquid detergent composition yields no more than 2% by volume visible phase separation when stored at 25°C for 21 days from the time of preparation, more preferably less than 0.1% by volume visible phase separation when stored at 25°C for 90 days from the time of preparation. Structured liquid detergent compositions according to the present invention are preferably "stable" according to these definitions.

Thus, when any structured composition according to the present invention comprises deflocculating polymer this may comprise one or more deflocculating polymer materials according to EP-A 346 995 and/or as recited herein below.

Generally, the amount of material of deflocculating polymer in a composition according to any aspect of the invention will be from 0.01% to 5.0% by weight in the structured composition, most preferably from 0.1% to 2.0%.

For example, EP-A-438 215 discloses preparation of acrylic acid telomers with a functional terminal group, using a secondary alcohol chain transfer agent which may, for example be a $\text{C}_6 - \text{C}_{12}$ monofunctional secondary alcohol. These materials are described as detergent additives, in particular sequestrants or anti-precipitants. The materials are produced using polymerisation initiators such as ditertiary butyl peroxide. In the description of various different possible initiators, there is mentioned lauryl peroxide.

Some specific kinds of deflocculating polymers which contain only one hydrophobic moiety and which is attached to an end position of a hydrophilic chain, are disclosed in EP-A-623 670.

- 5 Various sub-types are described for the deflocculating polymers in EP-A-623 670. However, many of those actually exemplified are thiol polyacrylates, that is to say, materials formed by polymerisation of acrylic acid in the presence of a hydrophobic chain transfer agent having from five to twenty five carbon atoms and a terminal-SH group, in a radical polymerisation process. Analogous materials having a thia linkage between the hydrophilic and hydrophobic parts of the molecule are disclosed in US-A-5 489 395, US-
10 A-5 489 397 and EP-A-691 399.

Another class of suitable deflocculating polymers comprises oligomers or polymers of formula (I) as disclosed in our international patent application WO-A-98/55576.

15

Ile Electrolyte

Although it is possible to form lamellar dispersions of surfactant in water alone, in many cases it is preferred for the aqueous continuous phase to contain dissolved electrolyte. As used herein, the term electrolyte means any ionic water-soluble material. However, in lamellar dispersions, not all the electrolyte is necessarily dissolved but may be suspended as particles of solid because the total electrolyte concentration of the liquid is higher than the solubility limit of the electrolyte. Mixtures of electrolytes also may be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being
20 substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally, between these two phases. In part, this may depend on processing, e.g. the order of addition of components. On the other hand, the terms 'salts' includes all organic and inorganic materials which may be included, other than surfactants and water, whether or not they are ionic, and this term encompasses the
25 sub-set of the electrolytes (water-soluble materials).
30

However, there is a limit to the size and amount of non-dissolved (i.e. suspended) electrolytes in these formulation which is consistent with the objective of clarity. The amount of small particles which are not visible as separate entities should be so low that

the bulk of the liquid remains substantially clear in accordance with the definition of the first aspect of the present invention. The amounts of relatively large particles (i.e. visible as separate entities) should be such that they have a pleasing visual effect like the aforementioned "visible solids".

5

The only restriction on the total amount of detergent-active material and electrolyte (if any) is that in the structured compositions of the invention, together they must result in formation of an aqueous lamellar dispersion. Thus, within the ambit of the present invention, a very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions, in order to obtain a stable liquid with the required structure will be fully within the capability of those skilled in the art.

10

Preferably, the structured compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided if of a kind and in an amount compatible with the other components and the structured composition is still in accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water-insoluble salt which may be present, may have detergency builder properties. In any event, it is preferred that structured compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the structured composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

20

25

If Detergency Builder

5 As already mentioned, water soluble inorganic detergency builders (if dissolved in the aqueous phase) are electrolytes but any solid material above the solubility limit will normally be suspended by the lamellar phase.

10 Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates. Phosphonate sequestrant builders may also be used.

15 Examples of non-phosphorous-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites, although there are restrictions with respect to the amount and volume fraction of solid particles which can be added while retaining substantial clarity.

20 In the context of inorganic builders, we prefer to include electrolytes which promote the solubility of other electrolytes, for example use of potassium salts to promote the solubility of sodium salts. Thereby, the amount of dissolved electrolyte can be increased considerably (crystal dissolution) as described in UK patent specification GB 1 302 543.

25 Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates, carboxymethyloxysuccinates, carboxymethyloxymalonates, ethylene diamine-N,N-disuccinic acid salts, polyepoxysuccinates, oxydiacetates, 30 triethylene tetramine hexa-acetic acid salts, N-alkyl imino diacetates or dipropionates, alpha sulpho- fatty acid salts, dipicolinic acid salts, oxidised polysaccharides, polyhydroxysulphonates and mixtures thereof.

Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamino-tetraacetic acid, nitrilo-triacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid, tartrate mono succinate and tartrate di succinate.

5

In the context of organic builders, it is also desirable to incorporate polymers which are only partly dissolved in the aqueous continuous phase. This allows a viscosity reduction (owing to the polymer which is dissolved whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved does not bring about the instability that would occur if substantially all were dissolved).

10

As for inorganic builders, the same restrictions apply with respect to the amount and volume fraction of non-dissolved polymer phase which can be added while retaining substantial clarity.

15

IIg Other Polymers

Examples of partly dissolved polymers include many of the polymer and co-polymer salts already known as detergency builders. For example, may be used (including building and non-building polymers) polyethylene glycols, polyacrylates, polymaleates, polysugars, polysugarsulphonates and co-polymers of any of these. Preferably, the partly dissolved polymer comprises a co-polymer which includes an alkali metal salt of a polyacrylic, polymethacrylic or maleic acid or anhydride. Preferably, structured compositions with these co-polymers have a pH of above 8.0. In general, the amount of viscosity-reducing polymer can vary widely according to the formulation of the rest of the structured composition. However, typical amounts are from 0.5 to 4.5% by weight.

20

25

It is further possible to include in the structured compositions of the present invention, alternatively, or in addition to the partly dissolved polymer, yet another polymer which is substantially totally soluble in the aqueous phase and has an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100 ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethylene glycol having an average molecular weight of 6,000; said second polymer having a molecular weight of at least 1,000.

30

The incorporation of the soluble polymer permits formulation with improved stability at the same viscosity (relative to the structured composition without the soluble polymer) or lower viscosity with the same stability. The soluble polymer can also reduce viscosity drift, even when it also brings about a viscosity reduction. Here, improved stability and lower viscosity mean over and above any such effects brought about by the deflocculating polymer.

It is especially preferred to incorporate the soluble polymer with a partly dissolved polymer which has a large insoluble component. That is because although the building capacity of the partly dissolved polymer will be good (since relatively high quantities can be stably incorporated), the viscosity reduction will not be optimum (since little will be dissolved). Thus, the soluble polymer can usefully function to reduce the viscosity further, to an ideal level.

The soluble polymer can, for example, be incorporated at from 0.05 to 20% by weight, although usually from 0.1 to 10% by weight of the total structured composition is sufficient, and especially from 0.2 to 3.5 - 4.5% by weight. It has been found that the presence of deflocculating polymer increase the tolerance for higher levels of soluble polymer without stability problems. A large number of different polymers may be used as such a soluble polymer, provided the electrolyte resistance and vapour pressure requirements are met. The former is measured as the amount of sodiumnitrolotriacetate (NaNTA) solution necessary to reach the cloud point of 100 ml of a 5% w/w solution of the polymer in water at 25°C, with the system adjusted to neutral pH, i.e. about 7. This is preferably effected using sodium hydroxide. Most preferably, the electrolyte resistance is 10 g NaNTA, especially 15g. The latter indicates a vapour pressure low enough to have sufficient water binding capability, as generally explained in the applicants' specification GB-A-2 053 249. Preferably, the measurement is effected with a reference solution at 10% by weight aqueous concentration, especially 18%.

Typical classes of polymers which may be used as the soluble polymer, provided they meet the above requirements, include polyethylene glycols, Dextran, Dextran sulphonates, polyacrylates and polyacrylate/maleic acid co-polymers.

The soluble polymer must have an average molecular weight of at least 1,000 but a minimum average molecular weight of 2,000 is preferred.

5 The use of partly soluble and the use of soluble polymers as referred to above in detergent compositions is described in our European patent specifications EP-A-301 882 and EP-A-301 883.

IIIh Hydrotropes

10 Although it is possible to incorporate minor amounts of hydrotropes such as lower alcohols (e.g. ethanol) or alkanolamines (e.g. triethanolamine), in order to ensure integrity of the lamellar dispersion we prefer that the structured compositions of the present invention are substantially free from hydrotropes. By hydrotrope is meant any water soluble agent which tends to enhance the solubility of surfactants in aqueous solution.

15 III Liquid detergents in general

The liquid detergent composition according the invention being either isotropic or structured may contain additional optional ingredients

20 Bleaches

The organic substance is a substance which forms a complex with a transiting metal, a complex being capable of catalysing bleaching at the substrate by atmospheric oxygen. In other words; as a complex it is an atmospheric oxygen bleach catalyst. Therefore, in order for a composition according to the invention to have bleaching performance, it is not necessary for it to contain a bleach or bleach system. However, bleaching performance may be further boosted by inclusion of a conventional bleach or bleach system.

30 Preferred are the oxygen bleaches and oxygen bleach systems. Indeed, many atmospheric oxygen bleach catalysts are also capable of catalysing bleach activity of such conventional oxygen bleaches and oxygen bleach systems. It is also possible in such cases, to include also, one or more conventional bleach catalysts which are not catalysts of atmospheric oxygen bleaching. In addition or in the alternative to oxygen

bleaches or bleach systems, halogen bleaches may be used, such as alkali metal hypohalites e.g. hypochlorites.

5 However, in the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt preferably with an activator, or as a peroxy acid compound.

10 In the case of the inorganic persalt bleaches, the activator makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low-temperature bleach systems and are well known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts as release active oxygen in solution, and activator is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for more effective bleaching action at lower
15 temperatures than the peroxy-bleach compound alone. The ratio by weight of the peroxy bleach compound to the activator is from about 15:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxy bleach compounds and activator may be varied between about 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients
20 forming the bleach system. Thus, the preferred level of the peroxy bleach compound in the composition is between 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 40%, most preferably between about 1% and about 5% by weight.

25 Typical examples of the suitable peroxybleach compounds are alkali metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, alkylhydroperoxides such as cumene hydroperoxide and t-butyl hydroperoxide, persilicates and perphosphates, of which sodium perborate is preferred. Activators for peroxybleach compounds have been amply described in the literature, including in British patent
30 specifications 836988, 855735, 907356, 907358, 907950, 1003310 and 1246339, U.S. Pat. No. 3332882 and 4128494, Canadian patent specification 844481 and South African patent specification 68/6344.

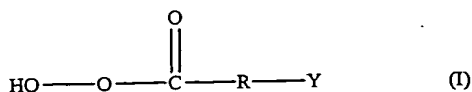
The exact mode of action of such activators is not known, but it is believed that peracids are formed by reaction of the activators with the inorganic peroxy compound, which peracids then liberate active-oxygen by decomposition.

- 5 They are generally compounds which contain N-acyl or O-acyl residues in the molecule and which exert their activating action on the peroxy compounds on contact with these in the washing liquor.

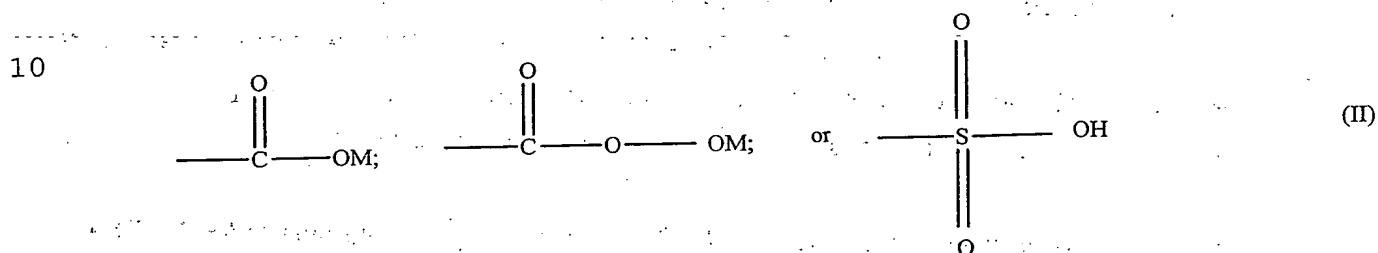
10 Typical examples of activators within these groups are polyacylated alkylene diamines, such N,N,N',N'-tetraacetylene diamine (TAED) and N,N,N',N'-tetraacetylmethylene diamine (TAMD); acylated glycolurils, such as tetraacetylglucuril (TAGU); triacetylcyanurate and sodium sulphophenyl ethyl carbonic acid ester.

15 A particularly preferred activator is N,N,N',N'-tetraacetylene diamine (TAED). The activator may be incorporated as fine particles or even in granular form, such as described in the applicants' UK patent specification GB 2 053 998 A. Specifically, it is preferred to have an activator of an average particle size of less than 150 micrometers, which gives significant improvement in bleach efficiency. The sedimentation losses, when using an activator with an average particle size of less than 150µm, are
20 substantially decreased. Even better bleach performance is obtained if the average particle size of the activator is less than 100 µm. However, too small a particle size can give increased decomposition and handling problems prior to processing. However, these particle sizes have to be reconciled with the requirements for dispersion in the solvent (it will be recalled that the aforementioned first product from requires particles
25 which are as small as possible within practical limits). Liquid activators may also be used, e.g. as hereinafter described.

The organic peroxyacid compound bleaches (which in some cases can also act as structurants/deflocculants) are preferably those which are solid at room temperature and
30 most preferably should have a melting point of at least 50°C. Most commonly, they are the organic peroxyacids and water-soluble salts thereof having the general formula

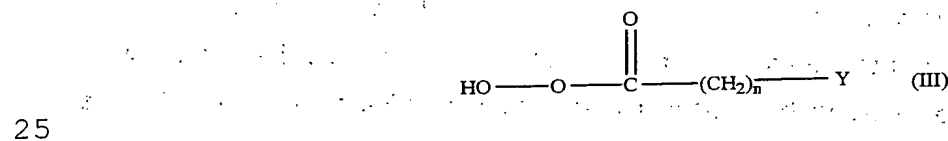


- 5 wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms; and Y is hydrogen halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example:

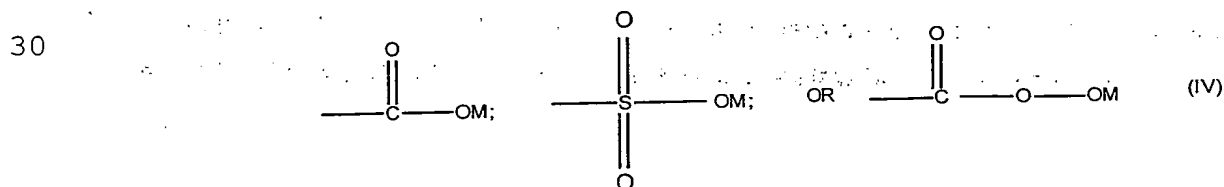


15 wherein M is H or a water-soluble, salt-forming cation.

The organic peroxyacids and salts thereof usable in the present invention can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula:

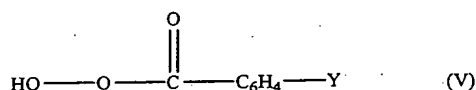


wherein Y can be H, -CH₃, -CH₂Cl,



And n can be an integer from 60 to 20. Peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids are the most preferred compounds of this type, particularly 1,12-diperoxydodecandioic acid (sometimes known as DPDA), 1,14-diperoxytetradecandioic acid and 1,16diperoxyhexadecandioic acid. Examples of other preferred compounds of this type are diperoxyazelaic acid, diperoxyadipic and diperoxysebacic acid.

- 10 When the organic peroxyacid is aromatic, a unsubstituted acid may have the general formula:



15

wherein Y is, for example hydrogen, halogen, alkyl or a group as defined for formulae (IV) above.

- 20 The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and saltes thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, diperoxyisophthalic acid, peroxy benzoic acids and ring-substituted peroxy benzoic acids, such as peroxy-alpha-naphthoic acid. A preferred aromatic peroxyacid is diperoxyisophthalic acid.
- 25

- Another preferred class of peroxygen compounds which can be incorporated to enhance dispensing/dispersibility in water are the anhydrous perborates described for that purpose in the applicants' European patent specification EP-A-217 454.
- 30

It is also preferred to include in the compositions, a stabiliser for the bleach or bleach system, for example ethylene diamine tetramethylene pholphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt

thereof, such as the Dequest range hereinbefore described. These stabilisers can be used in acid or salt form which as the calcium, magnesium, zinc or aluminium salt form. The stabiliser may be present at a level of up to about 1% by weight, preferably between about 0.1% and about 0.5% by weight.

5

Since many bleaches and bleach systems are unstable in aqueous liquid detergents and/or other interact unfavourably with other components in the composition, e.g. enzymes, they may for example be protected, e.g. by encapsulation or by formulating a structured liquid composition, whereby they are suspended in solid form.

10

Other Optional Ingredients

The compositions herein can further comprise a variety of optional ingredients. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C10-C16 alkanolamides can be incorporated into the compositions, typically at 1 %- 10% levels. The C10-C 14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing; adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgC12, MgSO4, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

20

25

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

30

By this means, ingredients such as the aforementioned, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable

surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers.

5

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron, copper and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-

10 substituted aromatic chelating agents and mixtures therein, all as hereinafter defined.

15

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

20

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties.

25

Liquid detergent compositions typically contain about 0.01% to about 5% of these agents.

One preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898,

30

Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered- ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430- 447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbon chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium. salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C 18-C40 ketones (e.g., stearone), etc.

The preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine.

Suds suppressors, when utilized, are preferably present in a "suds suppressing amount."

By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0.1% to about 5% of suds suppressor.

Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647 as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416 and U.S. Patent 4,291,071.

Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-

vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

5

Other than in the examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about". Similarly, all percentages are weight/weight percentages of the carbon dioxide unless otherwise indicated. Where the term "comprising" is used in the specification or claims, it is not intended to exclude any terms, steps or features not specifically recited.

10

The liquid detergent compositions according to the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.). As is generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

15

In typical washing compositions the level of the organic substance is such that the in-use level is from 0.05 μM to 50 mM, with preferred in-use levels for domestic laundry operations falling in the range 1 to 100 μM . Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching.

20

Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, and most preferably from 7 to 10.

Enzymes

25

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry application. Enzymes are included in the present detergent compositions for a variety of purposes, including removal of

protein-based, saccharide-based, or triglyceride-based stains, for the prevention of
refugee dye transfer, and for fabric restoration. Suitable enzymes include proteases,
amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin,
such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are
5 influenced by factors such as pH-activity and/or stability optima, thermostability, and
stability to active detergents, builders and the like. In this respect bacterial or fungal
enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at
10 levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective
amount" refers to any amount capable of producing a cleaning, stain removal, soil
removal, whitening, deodorizing, or freshness improving effect on substrates such as
fabrics. In practical terms for current commercial preparations, typical amounts are up to
about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the
15 detergent composition. Stated otherwise, the compositions herein will typically comprise
from 0.0001% to 10%, preferably from 0.001% to 5%, more preferably 0.005%-1% by
weight of a commercial enzyme preparation.

20 The Proteolyte Enzyme

Endopeptidases (proteolytic enzymes or proteases) of various qualities and origins and
having activity in various pH ranges of from 4-12 are available and can be used in the
instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which can
25 be obtained from particular strains of B. subtilis, B. lentus, B. amyloliquefaciens and B.
licheniformis, such as the commercially available subtilisins Savinase™, Alcalase™,
Release™, Kannase™ and Everlase™ as supplied by Novo Industri A/S, Copenhagen,
Denmark or Purafect™, PurafectOxP™ and Properase™ as supplied by Genencor
International. Chemically or genetically modified variants of these enzymes are included
30 such as described in WO-A-99/02632 pages 12 to 16 and in WO-A-99/20727 and also
variants with reduced allergenicity as described in WO-A-99/00489 and WO-A-99/49056.

The protease enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. It should be understood that the protease is present in the liquid detergent composition in a dissolved or dispersed form, i.e., the protease is not encapsulated to prevent the protease from the liquid composition. Instead the protease is more or less in direct contact with the liquid composition.

Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE™ by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE™ and SAVINASE™ from Novo and MAXATASE™ from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, and Protease B as disclosed in EP 303,761 A and EP 130,756 A. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A. Other preferred proteases include those of WO 9510591 A. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583.

Useful proteases are also described in PCT publications: WO 95/30010, WO 95/30011, WO 95/29979.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in EP-A-251446 (particularly pages 17, 24 and 98), and which is called herein

"Protease B", and in EP-A- 199404, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP-A-130756.

The preferred liquid laundry detergent compositions according to the present invention comprise at least 0.001% by weight, of a protease enzyme. However, an effective amount of protease enzyme is sufficient for use in the liquid laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Typically, the proteolytic enzyme content is up to 0.2%, preferably from $4 \times 10^{-5}\%$ to 0.06% by weight of the composition of pure enzyme.

Other Enzymes

The compositions of the invention may optionally contain one or more other enzymes.

For example, they may contain 10 - 20,000 LU per gram of the detergent composition of a lipolytic enzyme selected from the group consisting of Lipolase, Lipolase ultra, LipoPrime, Lipomax, Liposam, and lipase from *Rhizomucor miehei* (e.g. as described in EP-A-238 023 (Novo Nordisk).

The enzymatic detergent compositions of the invention further comprise 10 - 20,000 LU per gram, and preferably 50 - 2,000 LU per gram of the detergent composition, of an lipolytic enzyme. In this specification LU or lipase units are defined as they are in EP-A-258 068 (Novo Nordisk).

A further method of assessing the enzymatic activity is by measuring the reflectance at 460 nm according to standard techniques.

Suitable other enzymes for use in the compositions of the invention can be found in the enzyme classes of the esterases and lipases, (EC 3.1.1.*, wherein the asterisk denotes any number).

- 5 A characteristic feature of lipases is that they exhibit interfacial activation. This means that the enzyme activity is much higher on a substrate which has formed interfaces or micelles, than on fully dissolved substrate. Interface activation is reflected in a sudden increase in lipolytic activity when the substrate concentration is raised above the critical micel concentration (CMC) of the substrate, and interfaces are formed. Experimentally
10 this phenomenon can be observed as a discontinuity in the graph of enzyme activity versus substrate concentration. Contrary to lipases, however, cutinases do not exhibit any substantial interfacial activation.

- Suitable lipase enzymes for detergent usage include those produced by microorganisms
15 of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-
20 CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co. , Tagata, Japan; Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. LIPOLASE™ enzyme derived from Humicola lanyginosa and commercially available from Novo, see also EP 341,947, is a preferred lipase for use
25 herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 . Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

- Because of this characteristic feature, i.e. the absence of interfacial activation, we define
30 for the purpose of this patent application Cutinases as lipolytic enzymes which exhibit substantially no interfacial activation. Cutinases therefor differ from classical lipases in that they do not possess a helical lid covering the catalytic binding site. Cutinases belong to a different subclass of enzymes (EC 3.1.1.50) and are regarded to be outside the scope of the present invention.

Of main interest for the present invention are fungal lipases, such as those from *Humicola lanuginosa* and *Rhizomucor miehei*. Particularly suitable for the present invention is the lipase from *Humicola lanuginosa* strain DSM 4109, which is described in EP-A-305 216 (Novo Nordisk), and which is commercially available as Lipolase (TM). Also suitable are variants of this enzyme, such as described in WO-A-92/05249, WO-A-94/25577, WO-A-95/22615, WO-A-97/04079, WO-A-97/07202, WO-A-99/42566, WO-A-00/60063. Especially preferred is the variant D96L which is commercially available from Novozymes as Lipolase ultra, and the variant which is sold by Novozymes under the trade name LipoPrime.

The lipolytic enzyme of the present invention can usefully be added to the detergent composition in any suitable form, i.e. the form of a granular composition, a slurry of the enzyme, or with carrier material (e.g. as in EP-A-258 068 and the Savinase (TM) and Lipolase (TM) products of Novozymes). A good way of adding the enzyme to a liquid detergent product is in the form of a slurry containing 0.5 to 50 % by weight of the enzyme in a ethoxylated alcohol nonionic surfactant, such as described in EP-A-450 702 (Unilever).

The enzyme to be used in the detergent compositions according to the invention can be produced by cloning the gene for the enzyme into a suitable production organism, such as *Bacilli*, or *Pseudomonaceae*, yeasts, such as *Saccharomyces*, *Kluyveromyces*, *Hansenula* or *Pichia*, or fungi like *Aspergillus*. The preferred production organism is *Aspergillus* with especial preference for *Aspergillus oryzae*.

Other optional suitable enzymes which may be included alone or in combination with any other enzyme may, for example, be oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases. Suitable members of these enzyme classes are described in Enzyme nomenclature 1992: recommendations of the Nomenclature Committee of the International Union of Biochemistry and Molecular Biology on the nomenclature and classification of enzymes, 1992, ISBN 0-12-227165-3, Academic Press. The most recent information on the nomenclature of enzymes is available on the Internet through the ExPASy WWW server (<http://www.expasy.ch/>).

Examples of the hydrolases are carboxylic ester hydrolase, thiolester hydrolase, phosphoric monoester hydrolase, and phosphoric diester hydrolase which act on the ester bond; glycosidase which acts on O-glycosyl compounds; glycosylase hydrolysing N-glycosyl compounds; thioether hydrolase which acts on the ether bond; and

5 exopeptidases and endopeptidases which act on the peptide bond. Preferable among them are carboxylic ester hydrolase, glycosidase and exo- and endopeptidases. Specific examples of suitable hydrolases include (1) exopeptidases such as aminopeptidase and carboxypeptidase A and B and endopeptidases such as pepsin, pepsin B, chymosin, trypsin, chymotrypsin, elastase, enteropeptidase, cathepsin B, papain, chymopapain, 10 ficain, thrombin, plasmin, renin, subtilisin, aspergillopepsin, collagenase, clostripain, kallikrein, gastricsin, cathepsin D, bromelain, chymotrypsin C, urokinase, cucumisin, oryzin, proteinase K, thermomycolin, thermitase, lactocepin, thermolysin, bacillolysin. Preferred among them is subtilisin; (2) glycosidases such as α -amylase, β -amylase, glucoamylase, isoamylase, cellulase, endo-1,3(4)- β -glucanase (β -glucanase), xylanase, 15 dextranase, polygalacturonase (pectinase), lysozyme, invertase, hyaluronidase, pullulanase, neopullulanase, chitinase, arabinosidase, exocellobiohydrolase, hexosaminidase, mycodextranase, endo-1,4- β -mannanase (hemicellulase), xyloglucanase, endo- β -galactosidase (keratanase), mannanase and other saccharide gum degrading enzymes as described in WO-A-99/09127. Preferred among them are α - 20 amylase and cellulase; (3) carboxylic ester hydrolase including carboxylesterase, lipase, phospholipase, pectinesterase, cholesterol esterase, chlorophyllase, tannase and wax-ester hydrolase.

25 Examples of transferases and ligases are glutathione S-transferase and acid-thiol ligase as described in WO-A-98/59028 and xyloglycan endotransglycosylase as described in WO-A-98/38288.

30 Examples of lyases are hyaluronate lyase, pectate lyase, chondroitinase, pectin lyase, alginase II. Especially preferred is pectolyase, which is a mixture of pectinase and pectin lyase.

Examples of the oxidoreductases are oxidases such as glucose oxidase, methanol oxidase, bilirubin oxidase, catechol oxidase, laccase, peroxidases such as ligninase and those described in WO-A-97/31090, monooxygenase, dioxygenase such as lipoxygenase

and other oxygenases as described in WO-A-99/02632, WO-A-99/02638, WO-A-99/02639 and the cytochrome based enzymatic bleaching systems described in WO-A-99/02641.

- 5 Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo- peroxidase.

10

Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

15

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al.

20

A process for enhancing the efficacy of the bleaching action of oxidoreductases is by targeting them to stains by using antibodies or antibody fragments as described in WO-A-98/56885. Antibodies can also be added to control enzyme activity as described in WO-A-98/06812.

25

A preferred combination is a detergent composition comprising of a mixture of the protease of the invention and conventional detergent enzymes such as lipase, amylase and/or cellulase together with one or more plant cell wall degrading enzymes.

30

Suitable amylases include those of bacterial or fungal origin. Chemically or genetically modified variants of these enzymes are included as described in WO-A-99/02632 pages 18,19. Commercial cellulase are sold under the tradename Purastar™, Purastar OxAm™ (formerly Purafact Ox Am™) by Genencor; Termamyl™, Fungamyl™, Duramyl™, Natalase™, all available from Novozymes.

Amylases suitable herein include, for example, alfa-amylases described in GB 1,296,839 to Novo; RAPIDASE™, International Bio-Synthetics, Inc. and TERMAMYL™, Novo. FUNGAMYL™ from Novo is especially useful.

5

See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site- directed mutagenesis from one or more of the Baccillus amylases, especialy the Bacillus cc- amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

10

Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to WO 9402597, known as TERMAMYL™,

15

Particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL™. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo Or WO 9509909 A to Novo.

20

Suitable cellulases include those of bacterial or fungal origin. Chemically or genetically modified variants of these enzymes are included as described in WO-A-99/02632 page 17. Particularly useful cellulases are the endoglucanases such as the EGIII from *Trichoderma longibrachiatum* as described in WO-A-94/21801 and the E5 from *Thermomonospora fusca* as described in WO-A-97/20025. Endoglucanases may consist of a catalytic domain and a cellulose binding domain or a catalytic domain only. Preferred cellulolytic enzymes are sold under the tradename Carezyme™, Celluzyme™ and Endolase™ by Novo Nordisk A/S; Puradax™ is sold by Genencor and KAC™ is sold by Kao corporation, Japan.

25

30

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula* Solander. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A- 2.095.275 and DE-OS-2.247.832. CAREZYME™ (Novo) is especially useful. See also WO 9117243.

Detergent enzymes are usually incorporated in an amount of 0.00001% to 2%, and more preferably 0.001% to 0.5%, and even more preferably 0.01% to 0.2% in terms of pure enzyme protein by weight of the composition. Detergent enzymes are commonly employed in the form of granules made of crude enzyme alone or in combination with other components in the detergent composition. Granules of crude enzyme are used in such an amount that the pure enzyme is 0.001 to 50 weight percent in the granules. The granules are used in an amount of 0.002 to 20 and preferably 0.1 to 3 weight percent. Granular forms of detergent enzymes are known as Enzoguard™ granules, prills, marumes or T-granules. Granules can be formulated so as to contain an enzyme protecting agent (e.g. oxidation scavengers) and/or a dissolution retardant material. Other suitable forms of enzymes are liquid forms such as the "L" type liquids from Novo Nordisk, slurries of enzymes in nonionic surfactants such as the "SL" type sold by Novo Nordisk and microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP" and "CC".

The enzymes can be added as separate single ingredients (prills, granulates, stabilised liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates). Enzymes in liquid detergents can be stabilised by various techniques as for example disclosed in US-A-4 261 868 and US-A-4 318 818.

The detergent compositions of the present invention may additionally comprise one or more biologically active peptides such as swollenin proteins, expansins, bacteriocins and peptides capable of binding to stains.

The Primary Enzyme Stabiliser

The primary enzyme stabiliser is selected from boron-containing protease enzyme stabilisers, non-boron protease enzyme stabilisers and mixtures thereof.

5

Boron-containing Enzyme Stabilisers

Typical boron-based stabilisers include boron-based reversible stabilisers which comprise a boron compound and another substance capable of complexing with the boron compound to stabilise the enzyme in the composition but which complexes dissociate in the wash liquor to render the enzyme active.

10

Suitable boron compounds include sodium metaborate or sodium tetraborate (borax).

15

Typical substances which form a reversible complex with the boron compound including polyols such as glycerol, propylene glycol, and sorbitol. However, these are not enzyme stabilisers in the absence of the boron compound.

20

Typical inorganic boron sources are derivatives of boric acid including boric oxide, polyborates, orthoborates and metaborates or mixtures thereof. Preferred compounds are the alkali salts of the boric acid derivatives, such as sodium borate and borax.

Typical organic boron stabilisers are aromatic borate esters and boronic acid derivatives, such as alkyl, aryl and peptide boronic acids. Boronic acids are well-known as reversible inhibitors for subtilisine type of proteases.

25

Another boron-based stabilising system which may be used is the combination of boric acid or a boron compound capable of forming boric acid in the composition and a source of calcium ions, such as disclosed in EP-A-0 199 405.

30

Non-Boron Enzyme Stabilisers

Non-boron enzyme stabilisers include water soluble calcium compounds such as calcium chloride and/or formate and water soluble short chain carboxylic acids, as well as sources

of chlorine scavenge ions such as ammonium sulphates, bisulphites, thiosulphites, thiosulphate and thiols.

Mixtures of one or more boron- and or non-boron enzyme stabilisers may also be based.

5

The total amount of enzyme stabiliser or stabiliser system is typically from 0.001% to 10%, preferably from 0.005% to 7.5%, especially from 0.01% to 5% by weight of the total composition.

10 Many non-boron stabilisers are protein inhibitors from various sources and modified peptides (such as peptide aldehydes and peptide trifluoromethyl ketones). Suitable examples of these and other non-boron stabilisers include the following:-

15 WO-A-00/01826 discloses stabilized variants of Streptomycin subtilisin inhibitor (protein inhibitor + variants).

WO-A-98/13459 discloses liquid detergents containing proteolytic enzyme, peptide aldehydes and calcium ions.

20 EP-A-0 583 534 discloses liquid detergents containing a peptide aldehyde.

EP-A-0 583 535 describes liquid detergents containing a peptide trifluoromethylketone.

25 WO-A-97/00392 describes enzymatic compositions with improved storage stability of the enzymes contained therein are obtained by including an enzyme stabiliser, preferably by way of a particular process concerns the use of lignosulphonates.

WO-A-00/01831 describes a fusion between a subtilisin and streptomyces inhibitors variants).

30

Another suitable class of non-boron enzyme stabiliser comprises the reversible protease inhibitors of peptide or protein type, e.g. as disclosed in WO92/03529.

Further, our unpublished European Patent Application NO. 00202092.3 discloses other suitable non-boron enzyme stabilisers comprising at least one saccharide selected from disaccharides, trisaccharides and derivatives of either as well as mixtures of these disaccharides, trisaccharides and derivatives.

5

Yet others are disclosed in WO-A-98/13458, WO-A-98/13460, WO-A-98/13461, US-A-5 178 789, WO92/03529, WO-A-93/20175 and US-A-5 156 773.

The Organic Substance

10

The present invention requires the presence of an organic substance which forms a complex with a transition metal capable of catalysing atmospheric oxygen bleaches.

15

The organic substance may be incorporated in compositions according to the invention, either as a preformed complex of an organic ligand and a transition metal. Alternatively, it may be incorporated as the free organic substance. Without being bound by any theory, it is supposed that the organic substance can complex with a transition metal already present in the water or it might complex with a transition metal present in the substrate. The free organic substance may also be included as a composition of the free organic or a transition metal-substitutable metal-ligand complex, and a source of transition metal, whereby the complex is formed *in situ* in the medium. Generally speaking, the organic substance will usually be an organic ligand. It is preferred that the ligand is a pentadentate ligand or complex thereof.

20

25

The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

30

The transition metal complex preferably is of the general formula:



in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe (II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably from Fe(II)-(III)-(IV)-(V);

L represents the ligand, preferably N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

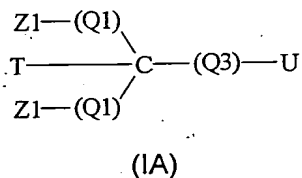
k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

Preferably, the complex is an iron complex comprising the ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane. However, it will be appreciated that the pretreatment method of the present invention may instead, or additionally, use other ligands and transition metal complexes, provided that the complex formed is capable of catalysing stain bleaching by atmospheric oxygen. Suitable classes of ligands are described below:

(A) Ligands of the general formula (IA):

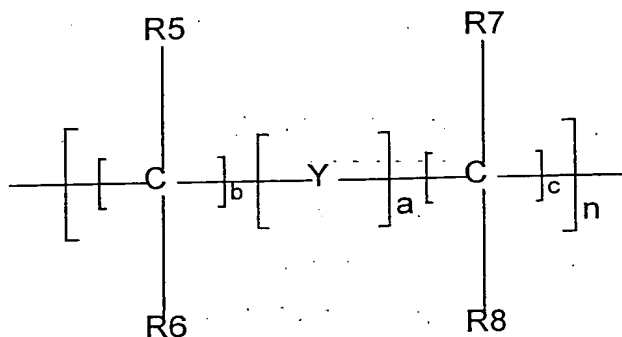


wherein

Z1 groups independently represent a coordinating group selected from hydroxy, amino, -NHR or -N(R)₂ (wherein R=C₁₋₆-alkyl), carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, a heterocyclic ring optionally substituted by one or more functional groups E or a heteroaromatic ring optionally substituted by one or more functional groups E, the

heteroaromatic ring being selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

5 Q1 and Q3 independently represent a group of the formula:



wherein

10

$5 \geq a+b+c \geq 1$; $a=0-5$; $b=0-5$; $c=0-5$; $n=0$ or 1 (preferably $n=0$);

Y independently represents a group selected from -O-, -S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein
 15 G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

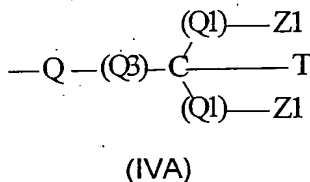
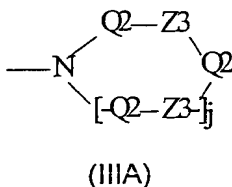
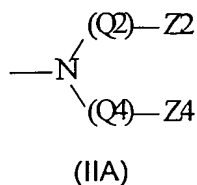
R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl,
 20 heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,
 or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C₁₋₆-alkylene optionally
 25 substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I;

T represents a non-coordinated group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl,

arylalkyl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E (preferably T = -H, -OH, methyl, methoxy or benzyl);

U represents either a non-coordinated group T independently defined as above or
5 a coordinating group of the general formula (IIA), (IIIA) or (IVA):



wherein

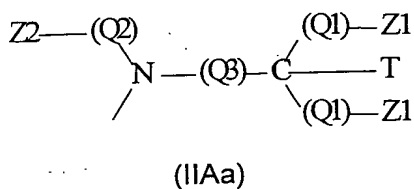
Q2 and Q4 are independently defined as for Q1 and Q3;

Q represents -N(T)- (wherein T is independently defined as above), or an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindol , oxazole and thiazole;

Z2 is independently defined as for Z1;

Z3 groups independently represent -N(T)- (wherein T is independently defined as above);

5 Z4 represents a coordinating or non-coordinating group selected from hydrogen, hydroxyl, halogen, -NH-C(NH)NH₂, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E, or Z4 represents a group of the general formula (IIAa):



and

$$1 \leq j < 4.$$

15 Preferably, Z1, Z2 and Z4 independently represent an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. More preferably, Z1, Z2 and Z4 independently represent groups selected from optionally substituted pyridin-2-yl, 20 optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl. Most preferred is that Z1, Z2 and Z4 each represent optionally substituted pyridin-2-yl.

25 The groups Z1, Z2 and Z4 if substituted, are preferably substituted by a group selected from C₁₋₄-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl. Preferred is that Z1, Z2 and Z4 are each substituted by a methyl group. Also, we prefer that the Z1 groups represent identical groups.

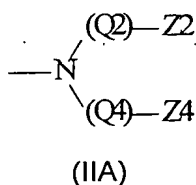
30 Each Q1 preferably represents a covalent bond or C1-C4-alkylene, more preferably a covalent bond, methylene or ethylene, most preferably a covalent bond.

Group Q preferably represents a covalent bond or C1-C4-alkylene, more preferably a covalent bond.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-C₀-C₂₀-alkyl, halo-C₀-C₂₀-alkyl, nitroso, formyl-C₀-C₂₀-alkyl, carboxyl-C₀-C₂₀-alkyl and esters and salts thereof, carbamoyl-C₀-C₂₀-alkyl, sulfo-C₀-C₂₀-alkyl and esters and salts thereof, sulfamoyl-C₀-C₂₀-alkyl, amino-C₀-C₂₀-alkyl, aryl-C₀-C₂₀-alkyl, C₀-C₂₀-alkyl, alkoxy-C₀-C₈-alkyl, carbonyl-C₀-C₆-alkoxy, and C₀-C₂₀-alkylamide. Preferably, none of R5-R8 is linked together.

Non-coordinated group T preferably represents hydrogen, hydroxy, methyl, ethyl, benzyl, or methoxy.

In one aspect, the group U in formula (IA) represents a coordinating group of the general formula (IIA):



According to this aspect, it is preferred that Z2 represents an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole, more preferably optionally substituted pyridin-2-yl or optionally substituted benzimidazol-2-yl.

It is also preferred, in this aspect, that Z4 represents an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole, more preferably optionally substituted pyridin-2-yl, or a non-coordinating group selected from hydrogen, hydroxy, alkoxy, alkyl, alkenyl, cycloalkyl, aryl, or benzyl.

In preferred embodiments of this aspect, the ligand is selected from:

1,1-bis(pyridin-2-yl)-N-methyl-N-(pyridin-2-ylmethyl)methylamine;

1,1-bis(pyridin-2-yl)-N,N-bis(6-methyl-pyridin-2-ylmethyl)methylamine;

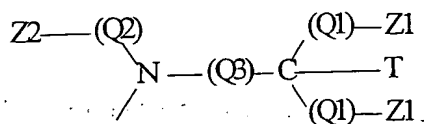
5 1,1-bis(pyridin-2-yl)-N,N-bis(5-carboxymethyl-pyridin-2-ylmethyl)methylamine;

1,1-bis(pyridin-2-yl)-1-benzyl-N,N-bis(pyridin-2-ylmethyl)methylamine; and

1,1-bis(pyridin-2-yl)-N,N-bis(benzimidazol-2-ylmethyl)methylamine.

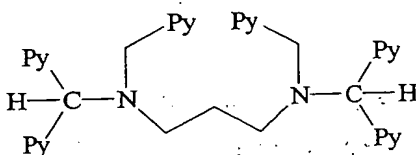
In a variant of this aspect, the group Z4 in formula (IIA) represents a group of the general

10 formula (IIAa):



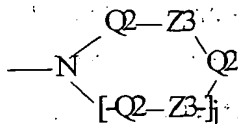
(IIAa)

15 In this variant, Q4 preferably represents optionally substituted alkylene, preferably -CH₂-CH(OH)-CH₂- or -CH₂-CH₂-CH₂-. In a preferred embodiment of this variant, the ligand is:



20 wherein -Py represents pyridin-2-yl.

In another aspect, the group U in formula (IA) represents a coordinating group of the general formula (IIIA):

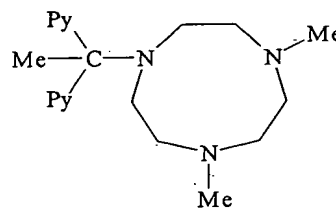
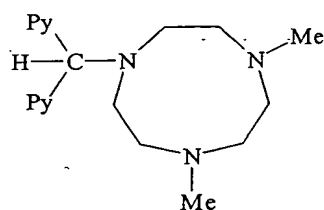


(III A)

wherein j is 1 or 2, preferably 1.

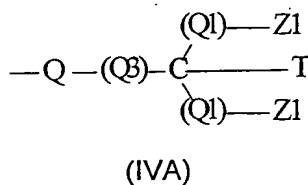
According to this aspect, each Q2 preferably represents $-(CH_2)_n-$ ($n=2-4$), and each Z3 preferably represents $-N(R)-$ wherein $R = -H$ or C_{1-4} -alkyl, preferably methyl.

In preferred embodiments of this aspect, the ligand is selected from:



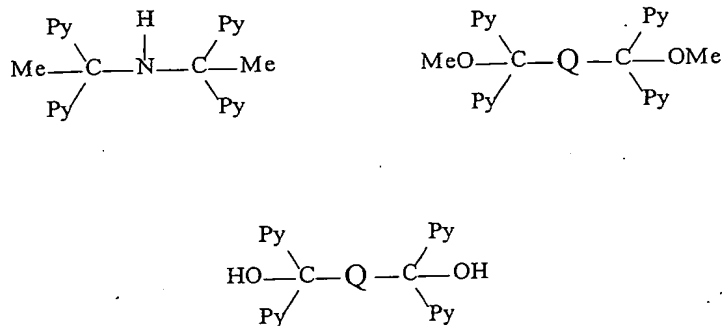
wherein -Py represents pyridin-2-yl.

In yet another aspect, the group U in formula (IA) represents a coordinating group of the general formula (IVA):



In this aspect, Q preferably represents $-N(T)-$ (wherein $T = -H$, methyl, or benzyl) or pyridin-diyl.

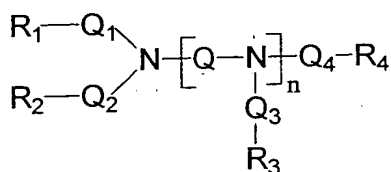
In preferred embodiments of this aspect, the ligand is selected from:



wherein -Py represents pyridin-2-yl, and -Q- represents pyridin-2,6-diyl.

5

(B) Ligands of the general formula (IB):



(IB)

10

wherein

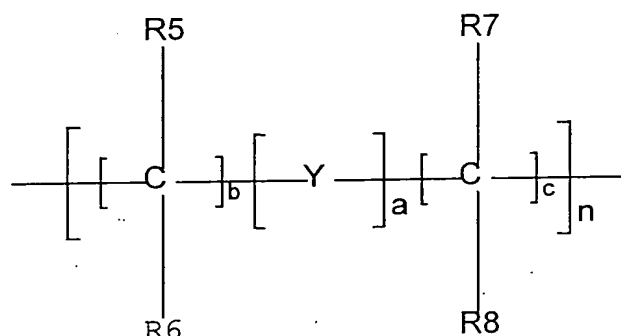
$n = 1$ or 2 , whereby if $n = 2$, then each $-\text{Q}_3-\text{R}_3$ group is independently defined;

15

R_1 , R_2 , R_3 , R_4 independently represent a group selected from hydrogen, hydroxyl, halogen, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$, $-\text{R}$ and $-\text{OR}$, wherein $\text{R} =$ alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E ,

20

Q_1 , Q_2 , Q_3 , Q_4 and Q independently represent a group of the formula:



wherein

5 $5 \geq a+b+c \geq 1$; $a=0-5$; $b=0-5$; $c=0-5$; $n=1$ or 2 ;

Y independently represents a group selected from -O-, -S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

10

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

15

or R5 together with R6, or R7 together with R8, or both, represent oxygen, or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C₁₋₆-alkylene optionally substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I;

20

provided that at least two of R₁, R₂, R₃, R₄ comprise coordinating heteroatoms and no more than six heteroatoms are coordinated to the same transition metal atom.

25

At least two, and preferably at least three, of R₁, R₂, R₃, R₄ independently represent a group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

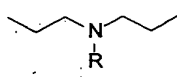
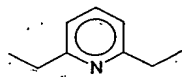
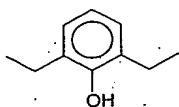
Preferably, substituents for groups R_1 , R_2 , R_3 , R_4 , when representing a heterocyclic or heteroaromatic ring, are selected from C_{1-4} -alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

- 5 The groups Q_1 , Q_2 , Q_3 , Q_4 preferably independently represent a group selected from $-CH_2-$ and $-CH_2CH_2-$.

Group Q is preferably a group selected from $-(CH_2)_{2-4}-$, $-CH_2CH(OH)CH_2-$,



optionally substituted by methyl or ethyl,



10

wherein R represents $-H$ or C_{1-4} -alkyl.

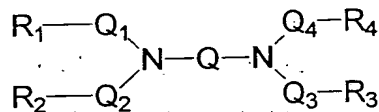
Preferably, Q_1 , Q_2 , Q_3 , Q_4 are defined such that $a=b=0$, $c=1$ and $n=1$, and Q is defined such that $a=b=0$, $c=2$ and $n=1$.

15

The groups R_5 , R_6 , R_7 , R_8 preferably independently represent a group selected from $-H$, hydroxy- C_0 - C_{20} -alkyl, halo- C_0 - C_{20} -alkyl, nitroso, formyl- C_0 - C_{20} -alkyl, carboxyl- C_0 - C_{20} -alkyl and esters and salts thereof, carbamoyl- C_0 - C_{20} -alkyl, sulfo- C_0 - C_{20} -alkyl and esters and salts thereof, sulfamoyl- C_0 - C_{20} -alkyl, amino- C_0 - C_{20} -alkyl, aryl- C_0 - C_{20} -alkyl, C_0 - C_{20} -alkyl, alkoxy- C_0 - C_8 -alkyl, carbonyl- C_0 - C_6 -alkoxy, and C_0 - C_{20} -alkylamide. Preferably, none of R_5 - R_8 is linked together.

20

In a preferred aspect, the ligand is of the general formula (IIB):



(IIB)

wherein

Q_1 , Q_2 , Q_3 , Q_4 are defined such that $a=b=0$, $c=1$ or 2 and $n=1$;

30

Q is defined such that $a=b=0$, $c=2,3$ or 4 and $n=1$; and
 $R_1, R_2, R_3, R_4, R_7, R_8$ are independently defined as for formula (I).

Preferred classes of ligands according to this aspect, as represented by formula (IIB)
5 above, are as follows:

(i) ligands of the general formula (IIB) wherein:

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from
carboxylate, amido, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$, hydroxyphenyl, an optionally substituted heterocyclic
10 ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine,
pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole,
isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

In this class, we prefer that:

15 Q is defined such that $a=b=0$, $c=2$ or 3 and $n=1$;

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from
optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally
substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted
quinolin-2-yl.

20 (ii) ligands of the general formula (IIB) wherein:

R_1, R_2, R_3 each independently represent a coordinating group selected from
carboxylate, amido, $-\text{NH}-\text{C}(\text{NH})\text{NH}_2$, hydroxyphenyl, an optionally substituted heterocyclic
ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine,
25 pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole,
isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_4 represents a group selected from hydrogen, C_{1-20} optionally substituted alkyl,
 C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein
 $\text{R}=\text{C}_{1-8}\text{-alkyl}$).

30 In this class, we prefer that:

Q is defined such that $a=b=0$, $c=2$ or 3 and $n=1$;

R_1, R_2, R_3 each independently represent a coordinating group selected from
optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally

substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_4 represents a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5} -furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted N^+Me_3 .

(iii) ligands of the general formula (IIB) wherein:

R_1 , R_4 each independently represent a coordinating group selected from carboxylate, amido, $-NH-C(NH)NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_2 , R_3 each independently represent a group selected from hydrogen, C_{1-20} optionally substituted alkyl, C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein $R=C_{1-8}$ -alkyl).

In this class, we prefer that:

Q is defined such that $a=b=0$, $c=2$ or 3 and $n=1$;

R_1 , R_4 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_2 , R_3 each independently represent a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5} -furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted N^+Me_3 .

Examples of preferred ligands in their simplest forms are:

N,N',N' -tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
 N -trimethylammoniumpropyl- N,N',N' -tris(pyridin-2-ylmethyl)-ethylenediamine;
 N -(2-hydroxyethylene)- N,N',N' -tris(pyridin-2-ylmethyl)-ethylenediamine;
 N,N,N',N' -tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine;
 N,N' -dimethyl- N,N' -bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine;
 N -(2-hydroxyethylene)- N,N',N' -tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;

- N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
5 N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'(2'-methoxy-ethyl-1)-ethylenediamine;
N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine;
N-(furan-2-yl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
10 N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine;
- N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
15 N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
- N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
20 N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
- N-methyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
25 N-ethyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
- 30 N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and
N-(2-methoxyethyl)-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

More preferred ligands are:

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

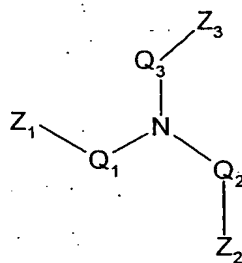
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

5 N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and

N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

(C) Ligands of the general formula (IC):

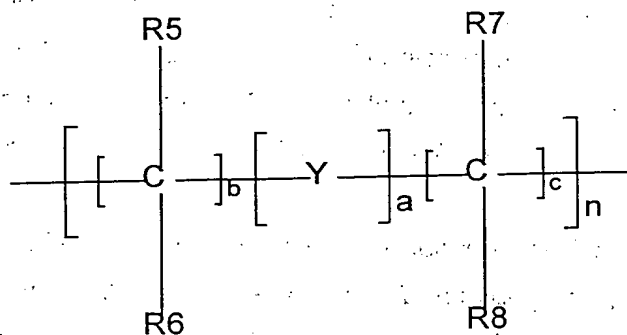


(IC)

wherein

15 Z₁, Z₂ and Z₃ independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

20 Q₁, Q₂, and Q₃ independently represent a group of the formula:



wherein

$$5 \geq a+b+c \geq 1; a=0-5; b=0-5; c=0-5; n=1 \text{ or } 2;$$

5 Y independently represents a group selected from -O-, -S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E; and

10 R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,
15 or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C₁₋₆-alkylene optionally substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I.

Z₁, Z₂ and Z₃ each represent a coordinating group, preferably selected from optionally
20 substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl. Preferably, Z₁, Z₂ and Z₃ each represent optionally substituted pyridin-2-yl.

Optional substituents for the groups Z₁, Z₂ and Z₃ are preferably selected from C₁₋₄-alkyl,
25 aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl, preferably methyl.

Also preferred is that Q₁, Q₂ and Q₃ are defined such that a=b=0, c=1 or 2, and n=1.

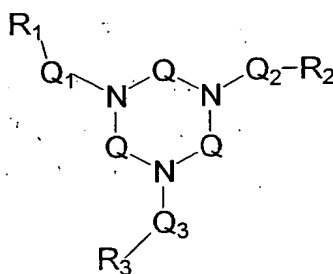
30 Preferably, each Q₁, Q₂ and Q₃ independently represent C₁₋₄-alkylene, more preferably a group selected from -CH₂- and -CH₂CH₂-.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-C₀-C₂₀-alkyl, halo-C₀-C₂₀-alkyl, nitroso, formyl-C₀-C₂₀-alkyl, carboxyl-C₀-C₂₀-alkyl

and esters and salts thereof, carbamoyl-C₀-C₂₀-alkyl, sulfo-C₀-C₂₀-alkyl and esters and salts thereof, sulfamoyl-C₀-C₂₀-alkyl, amino-C₀-C₂₀-alkyl, aryl-C₀-C₂₀-alkyl, C₀-C₂₀-alkyl, alkoxy-C₀-C₈-alkyl, carbonyl-C₀-C₆-alkoxy, and C₀-C₂₀-alkylamide. Preferably, none of R5-R8 is linked together.

Preferably, the ligand is selected from tris(pyridin-2-ylmethyl)amine, tris(3-methyl-pyridin-2-ylmethyl)amine, tris(5-methyl-pyridin-2-ylmethyl)amine, and tris(6-methyl-pyridin-2-ylmethyl)amine.

(D) Ligands of the general formula (ID):



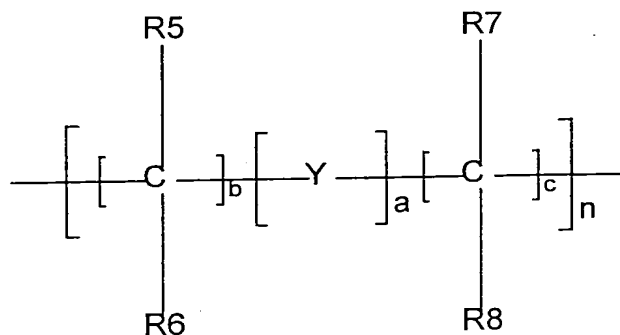
(ID)

wherein

R₁, R₂, and R₃ independently represent a group selected from hydrogen, hydroxyl, halogen, -NH-C(NH)NH₂, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E;

Q independently represent a group selected from C₂₋₃-alkylene optionally substituted by H, benzyl or C₁₋₈-alkyl;

Q₁, Q₂ and Q₃ independently represent a group of the formula:



wherein

5 $5 \geq a+b+c \geq 1$; $a=0-5$; $b=0-5$; $c=0-5$; $n=1$ or 2 ;

Y independently represents a group selected from -O-, -S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-, wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being
 10 optionally substituted by one or more functional groups E; and

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally
 15 substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,
 or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C₁₋₆-alkylene optionally substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I,
 20

provided that at least one, preferably at least two, of R₁, R₂ and R₃ is a coordinating group.

At least two, and preferably at least three, of R₁, R₂ and R₃ independently represent a
 25 group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline,

triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. Preferably, at least two of R_1 , R_2 , R_3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

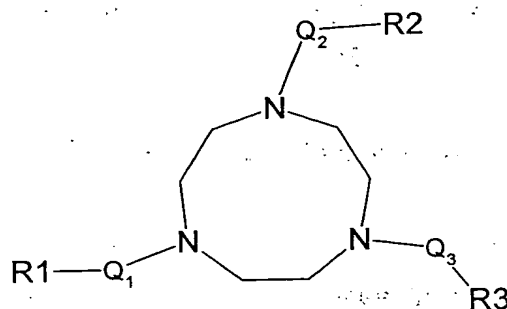
Preferably, substituents for groups R_1 , R_2 , R_3 , when representing a heterocyclic or heteroaromatic ring, are selected from C_{1-4} -alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

10 Preferably, Q_1 , Q_2 and Q_3 are defined such that $a=b=0$, $c=1,2,3$ or 4 and $n=1$. Preferably, the groups Q_1 , Q_2 and Q_3 independently represent a group selected from $-CH_2-$ and $-CH_2CH_2-$.

Group Q is preferably a group selected from $-CH_2CH_2-$ and $-CH_2CH_2CH_2-$.

15 The groups R_5 , R_6 , R_7 , R_8 preferably independently represent a group selected from $-H$, hydroxy- C_0-C_{20} -alkyl, halo- C_0-C_{20} -alkyl, nitroso, formyl- C_0-C_{20} -alkyl, carboxyl- C_0-C_{20} -alkyl and esters and salts thereof, carbamoyl- C_0-C_{20} -alkyl, sulfo- C_0-C_{20} -alkyl and esters and salts thereof, sulfamoyl- C_0-C_{20} -alkyl, amino- C_0-C_{20} -alkyl, aryl- C_0-C_{20} -alkyl, C_0-C_{20} -alkyl, 20 alkoxy- C_0-C_8 -alkyl, carbonyl- C_0-C_8 -alkoxy, and C_0-C_{20} -alkylamide. Preferably, none of R_5 - R_8 is linked together.

In a preferred aspect, the ligand is of the general formula (IID):



(IID)

wherein R₁, R₂, R₃ are as defined previously for R₁, R₂, R₈, and Q₁, Q₂, Q₃ are as defined previously.

Preferred classes of ligands according to this preferred aspect, as represented by formula (IID) above, are as follows:

(i) ligands of the general formula (IID) wherein:

R₁, R₂, R₃ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

In this class, we prefer that:

R₁, R₂, R₃ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

(ii) ligands of the general formula (IID) wherein:

two of R₁, R₂, R₃ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH₂, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

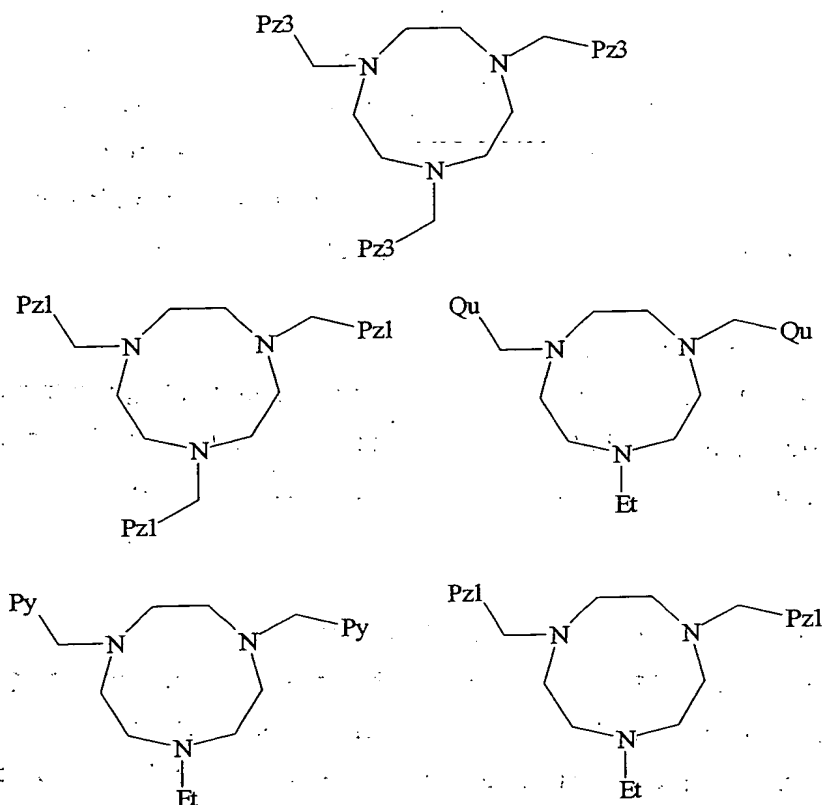
one of R₁, R₂, R₃ represents a group selected from hydrogen, C₁₋₂₀ optionally substituted alkyl, C₁₋₂₀ optionally substituted arylalkyl, aryl, and C₁₋₂₀ optionally substituted NR₃⁺ (wherein R=C₁₋₈-alkyl).

In this class, we prefer that:

two of R₁, R₂, R₃ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

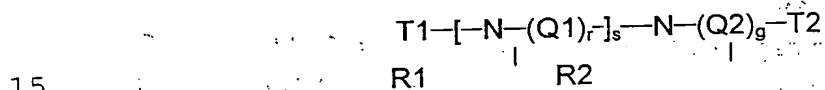
one of R1, R2, R3 represents a group selected from hydrogen, C₁₋₁₀ optionally substituted alkyl, C₁₋₅-furanyl, C₁₋₅ optionally substituted benzylalkyl, benzyl, C₁₋₅ optionally substituted alkoxy, and C₁₋₂₀ optionally substituted N⁺Me₃.

5 In especially preferred embodiments, the ligand is selected from:



wherein -Et represents ethyl, -Py represents pyridin-2-yl, Pz3 represents pyrazol-3-yl, Pz1
10 represents pyrazol-1-yl, and Qu represents quinolin-2-yl.

(E) Ligands of the general formula (IE):



(IE)

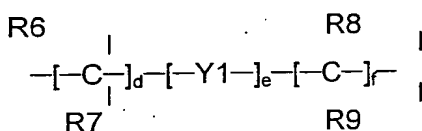
wherein

g represents zero or an integer from 1 to 6;

r represents an integer from 1 to 6;

s represents zero or an integer from 1 to 6;

5 Q1 and Q2 independently represent a group of the formula:



10

wherein

$5 \geq d+e+f \geq 1$; $d=0-5$; $e=0-5$; $f=0-5$;

each Y1 independently represents a group selected from -O-, -S-, -SO-, -SO₂-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N-,

15 wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

if $s > 1$, each $-\text{N}(\text{R1})-(\text{Q1})_r-$ group is independently defined;

20 R1, R2, R6, R7, R8, R9 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R6 together with R7, or R8 together with R9, or both, represent oxygen,

25 or R6 together with R8 and/or independently R7 together with R9, or R6 together with R9 and/or independently R7 together with R8, represent C₁₋₆-alkylene optionally substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I;

or one of R1-R9 is a bridging group bound to another moiety of the same general formula;

30

T1 and T2 independently represent groups R4 and R5, wherein R4 and R5 are as defined for R1-R9, and if $g=0$ and $s>0$, R1 together with R4, and/or R2 together with R5, may optionally independently represent =CH-R10, wherein R10 is as defined for R1-R9, or

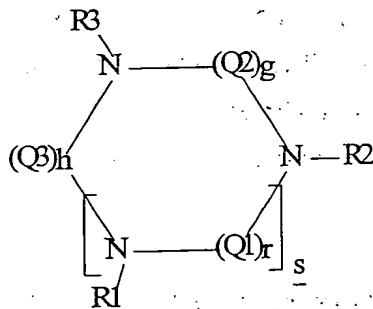
T1 and T2 may together (-T2-T1-) represent a covalent bond linkage when $s > 1$ and $g > 0$;

if T1 and T2 together represent a single bond linkage, Q1 and/or Q2 may independently represent a group of the formula: $=CH-[-Y1-]_e-CH=$ provided R1 and/or R2 are absent, and R1 and/or R2 may be absent provided Q1 and/or Q2 independently represent a group of the formula: $=CH-[-Y1-]_e-CH=$.

The groups R1-R9 are preferably independently selected from -H, hydroxy-C₀-C₂₀-alkyl, halo-C₀-C₂₀-alkyl, nitroso, formyl-C₀-C₂₀-alkyl, carboxyl-C₀-C₂₀-alkyl and esters and salts thereof, carbamoyl-C₀-C₂₀-alkyl, sulpho-C₀-C₂₀-alkyl and esters and salts thereof, sulphonamoyl-C₀-C₂₀-alkyl, amino-C₀-C₂₀-alkyl, aryl-C₀-C₂₀-alkyl, heteroaryl-C₀-C₂₀-alkyl, C₀-C₂₀-alkyl, alkoxy-C₀-C₈-alkyl, carbonyl-C₀-C₆-alkoxy, and aryl-C₀-C₆-alkyl and C₀-C₂₀-alkylamide.

One of R1-R9 may be a bridging group which links the ligand moiety to a second ligand moiety of preferably the same general structure. In this case the bridging group is independently defined according to the formula for Q1, Q2, preferably being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge, more preferably C₁₋₆-alkylene optionally substituted by C₁₋₄-alkyl, -F, -Cl, -Br or -I.

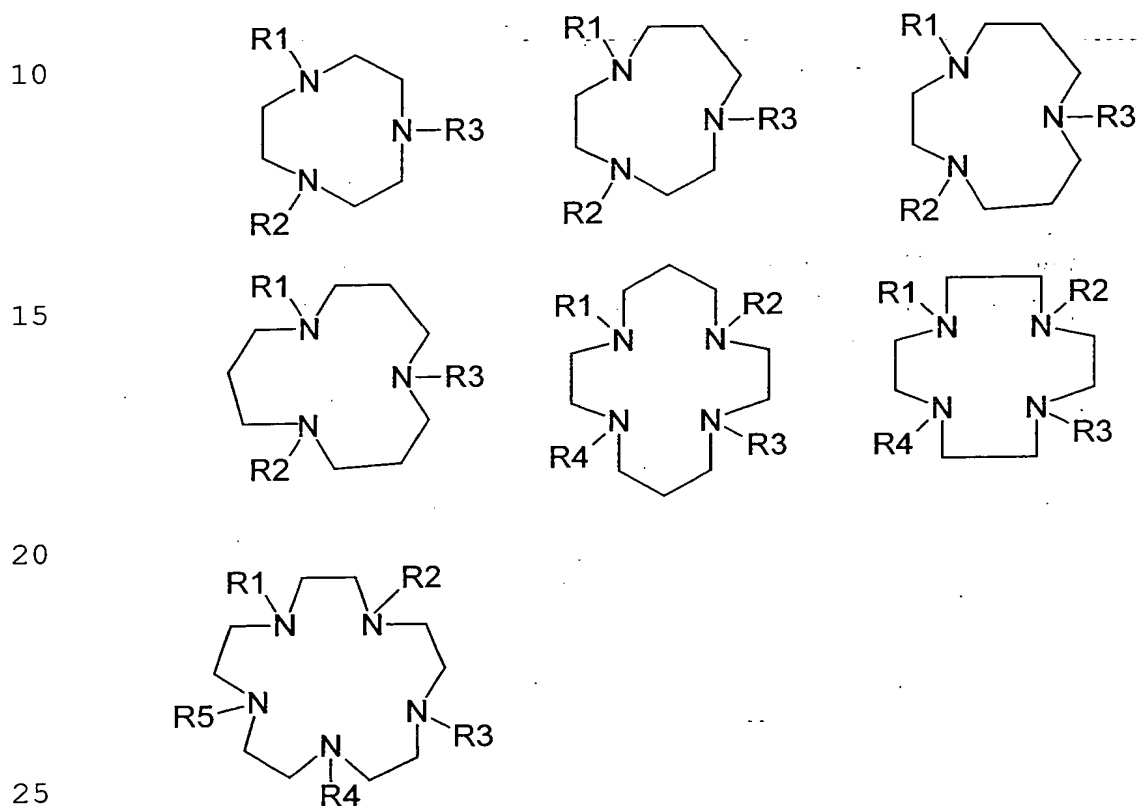
In a first variant according to formula (IE), the groups T1 and T2 together form a single bond linkage and $s > 1$, according to general formula (IIE):



(IIE)

wherein R3 independently represents a group as defined for R1-R9; Q3 independently represents a group as defined for Q1, Q2; h represents zero or an integer from 1 to 6; and $\underline{s}=s-1$.

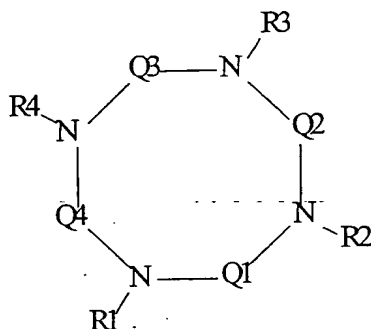
- 5 In a first embodiment of the first variant, in general formula (IIE), $\underline{s}=1, 2$ or 3; $r=g=h=1$; $d=2$ or 3; $e=f=0$; $R6=R7=H$, preferably such that the ligand has a general formula selected from:



- In these preferred examples, R1, R2, R3 and R4 are preferably independently selected from -H, alkyl, aryl, heteroaryl, and/or one of R1-R4 represents a bridging group bound to another moiety of the same general formula and/or two or more of R1-R4 together represent a bridging group linking N atoms in the same moiety, with the bridging group being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge, preferably heteroarylene. More preferably, R1, R2, R3 and R4 are independently selected from -H, methyl, ethyl, isopropyl, nitrogen-containing heteroaryl, or a bridging group bound to
- 30

another moiety of the same general formula or linking N atoms in the same moiety with the bridging group being alkylene or hydroxy-alkylene.

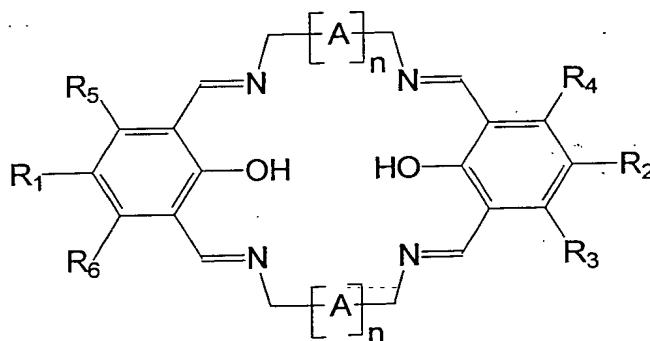
In a second embodiment of the first variant, in general formula (IIE), $s=2$ and $r=g=h=1$,
 5 according to the general formula:



In this second embodiment, preferably R1-R4 are absent; both Q1 and Q3 represent $=CH-[-Y1-]_e-CH=$; and both Q2 and Q4 represent $-CH_2-[-Y1-]_n-CH_2-$.

10

Thus, preferably the ligand has the general formula:



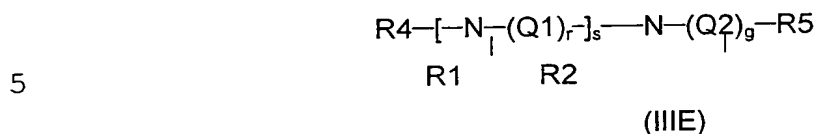
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wherein A represents optionally substituted alkylene optionally interrupted by a heteroatom; and n is zero or an integer from 1 to 5.

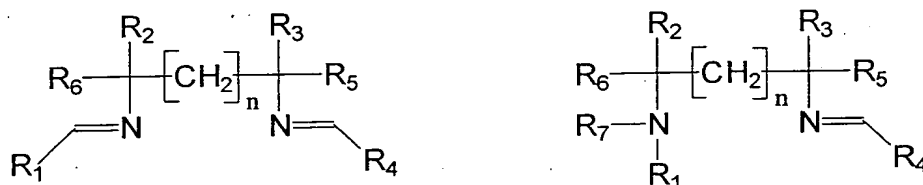
Preferably, R1-R6 represent hydrogen, $n=1$ and $A = -CH_2-$, $-CHOH-$, $-CH_2N(R)CH_2-$ or $-CH_2CH_2N(R)CH_2CH_2-$ wherein R represents hydrogen or alkyl, more preferably $A = -CH_2-$, $-CHOH-$ or $-CH_2CH_2NHCH_2CH_2-$.

20

In a second variant according to formula (IE), T1 and T2 independently represent groups R4, R5 as defined for R1-R9, according to the general formula (IIIE):



In a first embodiment of the second variant, in general formula (IIIE), $s=1$; $r=1$; $g=0$; $d=f=1$; $e=0-4$; $\text{Y1} = -\text{CH}_2-$; and R1 together with R4, and/or R2 together with R5, independently represent $=\text{CH-R10}$, wherein R10 is as defined for R1-R9. In one example, R2 together with R5 represents $=\text{CH-R10}$, with R1 and R4 being two separate groups. Alternatively, both R1 together with R4, and R2 together with R5 may independently represent $=\text{CH-R10}$. Thus, preferred ligands may for example have a structure selected from:



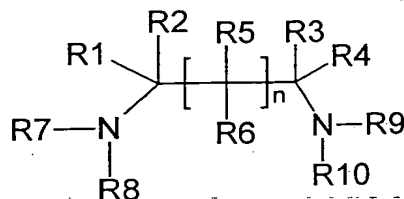
wherein $n = 0-4$.

Preferably, the ligand is selected from:



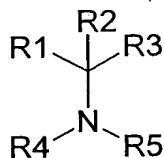
wherein R1 and R2 are selected from optionally substituted phenols, heteroaryl- $\text{C}_0\text{-C}_{20}$ -alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, heteroaryl- $\text{C}_0\text{-C}_{20}$ -alkyls, alkylaryl, aminoalkyl, alkoxy, more preferably R1 and R2 being selected from optionally substituted phenols, heteroaryl- $\text{C}_0\text{-C}_2$ -alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, nitrogen-heteroaryl- $\text{C}_0\text{-C}_2$ -alkyls.

In a second embodiment of the second variant, in general formula (IIIE), $s=1$; $r=1$; $g=0$; $d=f=1$; $e=1-4$; $Y1 = -C(R')(R'')$, wherein R' and R'' are independently as defined for $R1-R9$. Preferably, the ligand has the general formula:



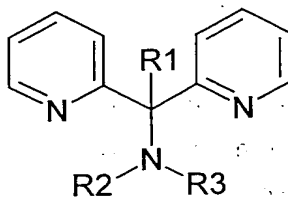
The groups $R1, R2, R3, R4, R5$ in this formula are preferably $-H$ or C_0-C_{20} -alkyl, $n=0$ or 1 , $R6$ is $-H$, alkyl, $-OH$ or $-SH$, and $R7, R8, R9, R10$ are preferably each independently selected from $-H$, C_0-C_{20} -alkyl, heteroaryl- C_0-C_{20} -alkyl, alkoxy- C_0-C_8 -alkyl and amino- C_{20} -alkyl.

In a third embodiment of the second variant, in general formula (IIIE), $s=0$; $g=1$; $d=e=0$; $f=1-4$. Preferably, the ligand has the general formula:



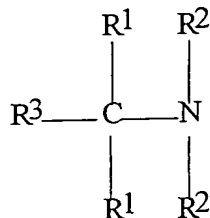
This class of ligand is particularly preferred according to the invention.

More preferably, the ligand has the general formula:



wherein $R1, R2, R3$ are as defined for $R2, R4, R5$.

In a fourth embodiment of the second variant, the ligand is a pentadentate ligand of the general formula (IVE):



(IVE)

5 wherein

each R^1 , R^2 independently represents $-\text{R}^4-\text{R}^5$,

R^3 represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or $-\text{R}^4-\text{R}^5$,

each R^4 independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic
10 amide, and

each R^5 independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

15 Ligands of the class represented by general formula (IVE) are also particularly preferred according to the invention. The ligand having the general formula (IVE), as defined above, is a pentadentate ligand. By 'pentadentate' herein is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex.

20 In formula (IVE), one coordinating hetero atom is provided by the nitrogen atom in the methylamine backbone, and preferably one coordinating hetero atom is contained in each of the four R^1 and R^2 side groups. Preferably, all the coordinating hetero atoms are nitrogen atoms.

25 The ligand of formula (IVE) preferably comprises at least two substituted or unsubstituted heteroaryl groups in the four side groups. The heteroaryl group is preferably a pyridin-2-yl group and, if substituted, preferably a methyl- or ethyl-substituted pyridin-2-yl group. More preferably, the heteroaryl group is an unsubstituted pyridin-2-yl group. Preferably, the heteroaryl group is linked to methylamine, and preferably to the N atom thereof, via a
30 methylene group. Preferably, the ligand of formula (IVE) contains at least one optionally

substituted amino-alkyl side group, more preferably two amino-ethyl side groups, in particular 2-(N-alkyl)amino-ethyl or 2-(N,N-dialkyl)amino-ethyl.

Thus, in formula (IVE) preferably R¹ represents pyridin-2-yl or R² represents pyridin-2-yl-methyl. Preferably R² or R¹ represents 2-amino-ethyl, 2-(N-(m)ethyl)amino-ethyl or 2-(N,N-di(m)ethyl)amino-ethyl. If substituted, R⁵ preferably represents 3-methyl pyridin-2-yl. R³ preferably represents hydrogen, benzyl or methyl.

Examples of preferred ligands of formula (IVE) in their simplest forms are:

(i) pyridin-2-yl containing ligands such as:

N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine;
 N,N-bis(pyrazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
 N,N-bis(imidazol-2-yl-methyl)-bis(pyridin-2-yl)methylamine;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
 N,N-bis(pyridin-2-yl-methyl)-bis(pyrazol-1-yl)methylamine;
 N,N-bis(pyridin-2-yl-methyl)-bis(imidazol-2-yl)methylamine;
 N,N-bis(pyridin-2-yl-methyl)-bis(1,2,4-triazol-1-yl)methylamine;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(4-sulphonic acid-phenyl)-1-
 aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-2-yl)-1-aminoethane;
 5 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-3-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-4-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-4-yl)-1-
 aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-3-yl)-1-
 10 aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-2-yl)-1-
 aminoethane;

(ii) 2-amino-ethyl containing ligands such as:

15 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;
 20 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;
 N,N-bis(pyridin-2-yl-methyl)-bis(2-amino-ethyl)methylamine;
 N,N-bis(pyrazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine;
 25 N,N-bis(imidazol-2-yl-methyl)-bis(2-amino-ethyl)methylamine;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine.

More preferred ligands are:

N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, hereafter referred to as N4Py.
 30 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, hereafter referred to as
 MeN4Py,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, hereafter
 referred to as BzN4Py.

In a fifth embodiment of the second variant, the ligand represents a pentadentate or hexadentate ligand of general formula (VE):



5

(VE)

wherein

each R^1 independently represents $-R^3-V$, in which R^3 represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and

10 V represents an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

W represents an optionally substituted alkylene bridging group selected from $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2-C_6H_4-CH_2-$, $-CH_2-C_6H_{10}-CH_2-$, and $-CH_2-C_{10}H_6-CH_2-$; and

15 R^2 represents a group selected from R^1 , and alkyl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and $N^+(R^4)_3$, wherein R^4 is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

20

The ligand having the general formula (VE), as defined above, is a pentadentate ligand or, if $R^1=R^2$, can be a hexadentate ligand. As mentioned above, by 'pentadentate' is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex. Similarly, by 'hexadentate' is meant that six hetero atoms can in principle coordinate to

25 the metal M ion. However, in this case it is believed that one of the arms will not be bound in the complex, so that the hexadentate ligand will be penta coordinating.

25

In the formula (VE), two hetero atoms are linked by the bridging group W and one coordinating hetero atom is contained in each of the three R^1 groups. Preferably, the

30 coordinating hetero atoms are nitrogen atoms.

30

The ligand of formula (VE) comprises at least one optionally substituted heteroaryl group in each of the three R^1 groups. Preferably, the heteroaryl group is a pyridin-2-yl group, in particular a methyl- or ethyl-substituted pyridin-2-yl group. The heteroaryl group is linked

to an N atom in formula (VE), preferably *via* an alkylene group, more preferably a methylene group. Most preferably, the heteroaryl group is a 3-methyl-pyridin-2-yl group linked to an N atom *via* methylene.

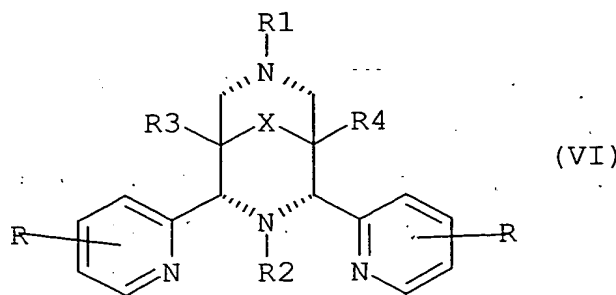
- 5 The group R^2 in formula (VE) is a substituted or unsubstituted alkyl, aryl or arylalkyl group, or a group R^1 . However, preferably R^2 is different from each of the groups R^1 in the formula above. Preferably, R^2 is methyl, ethyl, benzyl, 2-hydroxyethyl or 2-methoxyethyl. More preferably, R^2 is methyl or ethyl.

- 10 The bridging group W may be a substituted or unsubstituted alkylene group selected from $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$, $-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-$, and $-\text{CH}_2-\text{C}_{10}\text{H}_6-\text{CH}_2-$ (wherein $-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_{10}-$, $-\text{C}_{10}\text{H}_6-$ can be *ortho*-, *para*-, or *meta*- C_6H_4- , $-\text{C}_6\text{H}_{10}-$, $-\text{C}_{10}\text{H}_6-$). Preferably, the bridging group W is an ethylene or 1,4-butylene group, more preferably an ethylene group.

- 15 Preferably, V represents substituted pyridin-2-yl, especially methyl-substituted or ethyl-substituted pyridin-2-yl, and most preferably V represents 3-methyl pyridin-2-yl.

(F) Ligands of the classes disclosed in WO-A-98/39098 and WO-A-98/39406.

- 20 Another suitable class of ligand comprises the ligands having the formula (VI):



- 25 wherein each R is independently selected from: hydrogen, hydroxyl, $-\text{NH}-\text{CO}-\text{H}$, $-\text{NH}-\text{CO}-\text{C1-C4-alkyl}$, $-\text{NH}_2$, $-\text{NH}-\text{C1-C4-alkyl}$, and C1-C4-alkyl ;
 R1 and R2 are independently selected from:
 C1-C4-alkyl,

C6-C10-aryl, and,

a group containing a heteroatom capable of coordinating to a transition metal, preferably wherein at least one of R1 and R2 is the group containing the heteroatom;

R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and -
 5 (CH₂)_nC(O)OR₅

wherein R₅ is C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,

X is selected from C=O, -[C(R₆)₂]_Y- wherein Y is from 0 to 3 each R₆ is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

10

The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as RCOO⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻, NO₃⁻, F⁻, Cl⁻, Br⁻, or I⁻, with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z
 15 is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

15

Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from
 20 R⁷COO⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻ (in particular CF₃SO₃⁻), RSO₄⁻, SO₄²⁻, NO₃⁻, F⁻, Cl⁻, Br⁻, and I⁻, wherein R represents hydrogen or optionally substituted phenyl, naphthyl or C₁-C₄ alkyl.

20

It will be appreciated that the complex (A1) can be formed by any appropriate means,
 25 including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A1) under conditions of storage or use. Preferably, the complex is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution
 30 or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as FeSO₄ can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active complex. Thus, for example, the composition may formed

30

from a mixture of the ligand L and a metal salt MX_n in which preferably $n=1-5$, more preferably 1-3. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according the formula (A1).

Throughout the description and claims generic groups have been used, for example alkyl, alkoxy, aryl. Unless otherwise specified the following are preferred group restrictions that may be applied to generic groups found within compounds disclosed herein:

alkyl: C1-C6-alkyl,

alkenyl: C2-C6-alkenyl,

cycloalkyl: C3-C8-cycloalkyl,

alkoxy: C1-C6-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylene; 1,2-propylene; 1,3-propylene; 2,2-propylene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; and 1,4-butylene,

aryl: selected from homoaromatic compounds having a molecular weight under 300,

arylene: selected from the group consisting of: 1,2-benzene; 1,3-benzene; 1,4-benzene; 1,2-naphthalene; 1,3-naphthalene; 1,4-naphthalene; 2,3-naphthalene; phenol-2,3-diyl; phenol-2,4-diyl; phenol-2,5-diyl; and phenol-2,-6-diyl,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; pyrazinyl; triazolyl, pyridazinyl; 1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl; imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl; oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl,

heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,5-diyl; pyridin-2,6-diyl; pyridin-3,4-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; quinolin-2,8-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-1,3-diyl; pyrazol-3,5-diyl; triazole-3,5-diyl; triazole-1,3-diyl; pyrazin-2,5-diyl; and imidazole-2,4-diyl,

5 heterocycloalkyl: selected from the group consisting of: pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl; piperazinyl; hexamethylene imine; and oxazolidinyl,

amine: the group $-N(R)_2$ wherein each R is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C₆H₅; and phenyl, wherein when both R are C1-C6-alkyl both R together may form an -NC₃ to an -NC₅ heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

10

halogen: selected from the group consisting of: F; Cl; Br and I,

15 sulphonate: the group $-S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C₆H₅; Li; Na; K; Cs; Mg; and Ca,

sulphate: the group $-OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C₆H₅; Li; Na; K; Cs; Mg; and Ca,

20 sulphone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C₆H₅ and amine (to give sulphonamide) selected from the group: -NR'₂, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C₆H₅; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC₃ to an -NC₅ heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

25

carboxylate derivative: the group $-C(O)OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C₆H₅; Li; Na; K; Cs; Mg; and Ca,

30 carbonyl derivative: the group $-C(O)R$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C₆H₅ and amine (to give amide) selected from the group: -NR'₂, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C₆H₅; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form

an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

5 phosphonate: the group $-P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphate: the group $-OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

10 phosphine: the group $-P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5,

phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5; and amine (to give

15 phosphonamidate) selected from the group: $-NR'_2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.

20 Unless otherwise specified the following are more preferred group restrictions that may be applied to groups found within compounds disclosed herein:

alkyl: C1-C4-alkyl,

25 alkenyl: C3-C6-alkenyl,

cycloalkyl: C6-C8-cycloalkyl,

alkoxy: C1-C4-alkoxy,

30

alkylene: selected from the group consisting of: methylene; 1,2-ethylene; 1,3-propylene; butan-2-ol-1,4-diyl; and 1,4-butylene,

aryl: selected from group consisting of: phenyl; biphenyl, naphthalenyl; anthracenyl; and phenanthrenyl,

5 arylene: selected from the group consisting of: 1,2-benzene, 1,3-benzene, 1,4-benzene, 1,2-naphthalene, 1,4-naphthalene, 2,3-naphthalene and phenol-2,6-diyl,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl,

10 heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,6-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-3,5-diyl; and imidazole-2,4-diyl,

15 heterocycloalkyl: selected from the group consisting of: pyrrolidinyl; morpholinyl; piperidinyl; and piperazinyl,

amine: the group $-N(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

20 halogen: selected from the group consisting of: F and Cl,

sulphonate: the group $-S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

25 sulphate: the group $-OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

30 sulphone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'_2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

carboxylate derivative: the group $-C(O)OR$, wherein R is selected from hydrogen; Na; K; Mg; Ca; C1-C6-alkyl; and benzyl,

carbonyl derivative: the group: $-C(O)R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'_2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

- 5 phosphonate: the group $-P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl, benzyl; Na; K; Mg; and Ca,

phosphate: the group $-OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

10

phosphine: the group $-P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

15

phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: $-NR'_2$, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

20

Other compounds or ligands forming complexes with transition metals, and which are capable of catalysing bleaching by atmospheric oxygen, are suitable as organic substances in the liquid bleaching compositions of the present invention. These include the classes of complexes of a transition metal coordinated to a macropolycyclic ligand disclosed in WO-A-98/39098 and WO-A-98/39406.

25

Whilst the present invention is based on the catalytic bleaching of a substrate by atmospheric oxygen or air, it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in the liquid composition, if desired, provided that the chemical and physical stability of the composition is not thereby adversely affected to an unacceptable level. Therefore, by "substantially devoid of peroxygen bleach or peroxy-based or -generating bleach systems" is meant that the liquid bleaching composition contains from 0 to 50 %, preferably from 0 to 10 %, more preferably from 0 to 5 %, and optimally from 0 to 2 % by molar weight on an oxygen basis, of peroxygen bleach or peroxy-based or -generating bleach systems. Preferably,

30

however, the liquid bleaching composition will be wholly devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

Thus, at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of the substrate is effected by oxygen sourced from the air.

According to the fourth aspect, the organic substance in the liquid bleaching composition may be contacted to the textile fabric in any suitable manner. For example, it may be applied in a liquor that is then dried, for example as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. Other suitable means of contacting the organic substance in liquid form to the textile may be used, as further explained below.

Any suitable textile that is susceptible to bleaching or one that one might wish to subject to bleaching may be used. Preferably the textile is a laundry fabric or garment.

In a preferred embodiment of the fourth aspect, the method is carried out on a laundry fabric using an aqueous treatment liquor. In particular, the treatment may be effected in a wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent bleach wash liquid. In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

The bleaching method of the fourth aspect may be carried out by simply leaving the substrate in contact with the organic substance in the liquid bleaching composition for a sufficient period of time. Preferably, however, the organic substance is in an aqueous medium, and the aqueous medium on or containing the substrate is agitated.

In a preferred embodiment of the fourth aspect, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

In a particularly preferred embodiment the method according to the fourth aspect is carried out on a laundry fabric using aqueous treatment liquor. In particular the treatment may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent

wash liquor. Preferably, the organic substance is delivered into the wash liquor from a liquid concentrate.

5 The present invention is not limited to those circumstances in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In these circumstances it is envisaged that the organic substance in liquid composition can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement which is being employed, such as a brush, bat or dolly, or from any suitable applicator for liquid compositions.

10 Suitable pre-treatment means for application of the organic substance from the liquid composition to the textile material prior to the main wash include sprays, pens, roller-ball devices and impregnated cloths or cloths containing microcapsules. Such means are well known in the analogous art of deodorant application and/or in spot treatment of textiles.

15 Similar means for application are employed in those embodiments where the organic substance in liquid composition is applied after the main washing and/or conditioning steps have been performed, e.g. prior to or after ironing or drying of the cloth. For example, the organic substance in liquid composition may be applied using tapes, sheets or sticking plasters coated or impregnated with the substance, or containing
20 microcapsules of the substance. The organic substance in liquid composition may for example be incorporated into a drier sheet so as to be activated or released during a tumble-drier cycle, or the organic substance in liquid composition can be provided in an impregnated or microcapsule-containing sheet so as to be delivered to the textile when ironed.

25 The invention will now be further illustrated by way of the following non-limiting examples:

EXAMPLES

Preparation of ligand and Complex

- 5 This example describes a synthesis of an atmospheric oxygen bleaching catalyst.

(i) Preparation of MeN4Py ligand (A):

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, MeN4Py, was prepared according to the procedure found in EP 0 909 809 A.

10

(ii) Synthesis of the complex FeMeN4PyCl₂ (B):

MeN4Py ligand (33.7 g; 88.5mmoles) was dissolved in 500ml dry methanol. Small portions of FeCl₂·4H₂O (0.95eq; 16.7g; 84.0mmoles) were added, yielding a clear red solution. After addition, the solution was stirred for 30 minutes at room temperature, after which the methanol was removed (rotary-evaporator). The dry solid was ground and 150 ml of ethylacetate was added and the mixture was stirred until a fine red powder was obtained. This powder was washed twice with ethyl acetate, dried in the air and further dried under vacuum (40 °C). El. Anal. Calc. for [Fe(MeN4py)Cl]Cl·2H₂O: C 53.03; H 5.16; N 12.89; Cl 13.07; Fe 10.01%. Found C 52.29/ 52.03; H 5.05/5.03; N 12.55/12.61; Cl: 12.73/12.69; Fe: 10.06/10.01%.

20

The following example formulations were prepared:

Ingredient	Parts by Weight			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
LAS-acid	7.01	7.06	6.97	7.04
sLES	13.11	13.12	13.1	13.03
Coconut fatty acid	1.01	1	1.01	1
NI 7EO	8.21	8.26	8.27	8.24
NaOH	0.73	0.59	0.27	0.15
Monoethanolamine	0.25	0.25	0.26	0.25
Sodium Citrate 2aq	3.98	4.01	3.99	4.01
Sodium tetraborate. 5aq	3.8	3.82	3.8	2.49
Sorbitol	4.05	-	-	-
PPG	4.43	4.49	2.31	2.3
Fluorescer	0.26	0.27	0.25	0.25
Protease Enzyme (4%)	0.4	0.4	0.4	0.4
Minors	0.63	0.64	0.61	0.61

5 PPG = propylene glycol

In all cases, the pH of the composition was 7.2.

10 The % residual activity (RA) of the protease enzyme after storage at 37°C was measured up to 56 days for the compositions of Examples 1-4 alone (controls), for the same compositions with 0.1% by weight of the complex B added and the same compositions with only the free ligand A added (on a mole equivalent basis of the amount of the ligand in 0.1% by weight of complex B).

15 The results below show an improvement in stability with both free ligand A and complex B. Further, they show an improvement with or without sorbitol present.

Example 1

5

Days	Control	+ 0.1% Complex B	+ 0.1% mole equiv. Ligand A
	Avg. RA (%)	Avg.RA (%)	Avg.RA (%)
0	100.0	100.0	100.0
3	74	91	89
7	63	90	73
14	43	88	59
28	21	89	49
56	3	77	25

Example 2

Days	Control	+ 0.1% Complex B	+ 0.1% mole equiv. Ligand A
T	Avg. RA (%)	Avg.RA (%)	Avg.RA (%)
0	100.0	100.0	100.0
3	81.3	93.7	85.0
7	50.9	84.1	63.9
14	25.6	93.9	48.8
28	11.3	79.0	38.0
56	2.0	71.3	18.4

10

15

Example 3

Days	Control	+ 0.1% Complex B	+ 0.1% mole equiv. Ligand A
	Avg. RA (%)	Avg.RA (%)	Avg.RA (%)
0	100.0	100.0	100.0
3	61.8	92.2	70.7
7	33.6	87.1	63.1
14	13.7	80.4	46.9
28	7.1	89.7	29.3
56	1.4	75.4	13.0

5

Example 4

Days	Control	+ 0.1% Complex B	+ 0.1% mole equiv. Ligand A
	Avg. RA (%)	Avg.RA (%)	Avg.RA (%)
0	100.0	100.0	100.0
3	58.4	79.0	72.0
7	31.8	74.0	53.0
14	10.4	64.9	32.3
28	5.0	59.8	18.6
56	0.0	48.7	5.2

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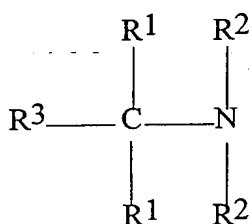
CLAIMS:

1. An aqueous liquid cleaning composition having a pH of at least 7, preferably from 7 to 11, more preferably from 7 to 10 and comprising a proteolytic enzyme and a primary stabiliser therefor, the composition further comprising an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen.
2. A liquid cleaning composition according to claim 1, wherein the primary enzyme stabiliser comprises a boron enzyme stabiliser.
3. A liquid cleaning composition according to claim 2, wherein the boron enzyme stabiliser is selected from boric acid, sodium metaborate, sodium tetraborate and mixtures thereof.
4. A liquid cleaning composition according to any of claims 1-3, wherein the primary enzyme stabiliser comprises a non-boron enzyme stabiliser.
5. A liquid cleaning composition comprising a proteolytic enzyme and a non-boron primary stabiliser therefor, the composition further comprising an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen, the composition being substantially free of boron enzyme stabiliser.
6. A liquid cleaning composition according to claim 4 or claim 5, wherein the non-boron enzyme stabiliser is selected from sources of calcium ions, modified peptides and mixtures thereof.
7. A liquid cleaning composition according to any preceding claim, comprising from 0.001% to 10% preferably from 0.005% to 7.5% by weight of the primary enzyme stabiliser.

8. A liquid cleaning composition according to claim 1, wherein the proteolytic enzyme is selected from subtilisins and modified bacterial serine proteases.

9. A liquid cleaning composition according to either preceding claim, comprising from 0.005 to 0.1 AU per gram of the composition of proteolytic enzyme.

10. A liquid cleaning composition according to any claim, preceding wherein the organic substance comprises a pentadentate ligand of the general formula (B):



(B)

wherein

each R^1 , R^2 independently represents $-\text{R}^4-\text{R}^5$,

R^3 represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or $-\text{R}^4-\text{R}^5$,

each R^4 independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and

each R^5 independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

11. A liquid cleaning composition according to claim 9, wherein the ligand is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane.

12. A liquid cleaning composition according to any preceding claim, having a pH value in the range from pH 6 to 11.

13. A liquid cleaning composition according to claim 11, wherein the composition has a pH value in the range from pH 7 to 10.

14. A liquid cleaning composition according to any preceding claim, wherein the medium is substantially devoid of a transition metal sequestrant.

15. A liquid cleaning composition according to any preceding claim, wherein the medium further comprises a surfactant.

16. A liquid cleaning composition according to any of claims 1 to 7, wherein the medium further comprises a builder.

17. A liquid cleaning composition according to any of claims 1 to 8, wherein the organic substance comprises a preformed complex of a ligand and a transition metal.

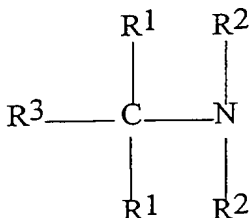
18. A liquid cleaning composition according to any of claims 1 to 8, wherein the organic substance comprises a free ligand that complexes with a transition metal present in the water.

19. A liquid cleaning composition according to any of claims 1 to 8, wherein the organic substance comprises a free ligand that complexes with a transition metal present in the substrate.

20. A liquid cleaning composition according to any of claims 1 to 8, wherein the organic substance comprises a composition of a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

21. A method of cleaning a substrate comprising applying to the substrate, an aqueous liquid cleaning composition according to any preceding claim.

22. A method according to claim 21, wherein the organic substance comprises a pentadentate ligand of the general formula (B):



(B)

wherein

each R^1 , R^2 independently represents $-R^4-R^5$,5 R^3 represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or $-R^4-R^5$,each R^4 independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and10 each R^5 independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

23. A method according to claim 22, wherein the ligand is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane.

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24. Use of an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by the atmospheric oxygen, as a secondary enzyme stabiliser in an aqueous liquid detergent composition comprising a proteolytic enzyme and a primary stabiliser therefor.

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ABSTRACT:**LIQUID CLEANING COMPOSITONS AND THEIR USE**

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The invention relates to an aqueous liquid cleaning composition comprising a proteolytic enzyme and a primary enzyme stabiliser therefor, the composition further comprising an organic substance which forms a complex with a transition metal, the complex being capable of catalysing bleaching of a substrate by atmospheric oxygen. The composition

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has a pH from 7 to 11, more preferably from 7 to 10 and/or is substantially free from boron primary enzyme stabiliser.

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